# COMBUSTION & FLAME

*Quarterly Journal of The Combustion Institute*

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VOLUME 11 NO. 3 SEPTEMBER 1958


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*Published quarterly. Annual subscription including postage—U.K. £5 5s. 0d.; U.S.A. $16.00. Combined subscription with* FUEL*—U.K. £8 8s. 0d.; U.S.A. $25.00. Editorial Offices, Showroom, Binding and Trade Departments:* 4-5 Bell Yard, Temple Bar, London, W.C.2. *Publishing and Advertising Offices:* 88 Kingsway, London, W.C.2. *Telephone:* Holborn 6900. *U.S.A. Distributors: Interscience Publishers Inc., 250 Fifth Avenue, New York 1, N.Y.*

BUTTERWORTHS SCIENTIFIC PUBLICATIONS

# *Hydroxyl Concentrations in Rich Hydrogen–Air Flames Held on Porous Burners*

W. E. KASKAN

*Cooled porous metal burners are shown to have great advantages for the study of chemical kinetics in flames and flame gases. A method is described for determining quantitatively the concentration of the* OH *radical in flame gases and measurements are reported for rich hydrogen-air flames. The* OH *concentrations near the flame are shown to be always in considerable excess of the calculated equilibrium concentrations. These excess concentrations decay in a manner which can be explained by assuming that the reaction*

$$OH + H_2 \rightleftharpoons H_2O + H$$

*is fast in both directions so that the* OH/H *ratio is always the equilibrium ratio. Both radicals then decay by the three body recombinations of* H *with itself and with* OH *to form* $H_2$ *and* $H_2O$. *It is shown that for the slower flames the diffusion of the radicals can lead to erroneous results.*

PRESENT knowledge of the chemistry of combustion processes is severely limited by the lack of knowledge of free radicals in flames, their concentrations and reactions. Free radicals are in general difficult to measure quantitatively, but the spectroscopic determination of hydroxyl, OH, is possible and in fact has been carried out in flames by various investigators[1].

Previous work has been hampered by the lack of a premixed flame with a geometry suitable for optical studies. However, the development of the cooled porous metal burner has greatly enlarged our capabilities for the study of reaction kinetics of premixed flames and flame gases. The characteristics of this burner have been described[2–4]. Briefly it consists of a pipe capped with a plug of uniform porous metal provided with some form of cooling. The combustible mixture is forced through the porous plug and emerges as a stream of (ideally) uniform velocity. If this velocity is less than the normal burning velocity, a flame ignited in this stream will burn through the mixture and stabilize itself as a flat flame burning in close proximity to the burner surface. In so doing the flame transfers to the burner an amount of heat which is determined by the mass velocity of the gas and its composition and pressure. This heat is conducted through the porous metal to the cooling coils where it is carried away by the cooling water. The flame temperature is lowered from the adiabatic value as a consequence of this loss of heat and data have been reported for the dependence of the final temperature on mass velocity[4].

The use of these burners provides three major advantages for the study of premixed flames: (*1*) they can produce flat, quite uniform, one-dimensional flames with flow perpendicular to the flame surface; (*2*) they provide flames of high stability, since the flame position is determined by the position of the burner surface; and (*3*) they allow the variation of flame temperature independent of composition.

Because of these advantages, it was thought worthwhile to investigate the OH radical in flames burning on porous burners to see what could be learned of its concentrations and reactions. The present paper concerns measurements in rich hydrogen–air flames. At atmospheric pressure the reaction zones of hydrogen–air flames are too thin to allow dissection. However, as will be shown below and as has been found by other investigators, the hot gases produced by these flames, whether on porous burners[5] or not[6], are sufficiently removed from complete thermodynamic equilibrium to allow kinetic studies to be made. These studies are further facilitated by the fact that the hot gases constitute a region of nearly constant temperature.

## SPECTROSCOPIC METHOD

OH can be determined by measuring the absorption in the ultraviolet $^2\Pi$–$^2\Sigma$ band. This spectrum has been exhaustively analysed[7] and a convenient reproduction is available[8]. The $f$ numbers of a number of lines in the 3064 0—0 band have been measured[9] and later corrected[10]. Line shapes indicating some pressure broadening in a mixture of $2H_2O + O_2$ at 1473°K have been reported[9], but it has been shown, using the same data, that the pressure broadening under these conditions is actually very small[11]. Consequently in the present work it has been assumed that the absorption lines have a pure Doppler shape. The most important consequence of this assumption is that with it the absorption coefficient becomes independent of pressure.

The method used to determine OH is the line absorption method[12, 13], in which a narrow emission line from a discharge in water vapour is absorbed by the broader absorption line in the flame. This method requires: that the line shapes in emission and absorption be known; that the integrated absorption coefficient be known; that the resolving power of the spectrograph be high enough to separate the lines to be used from all other lines, but it need not be high enough to resolve the line shapes. This last requirement is easily met, but the other two are not.

The method becomes particularly simple if the emission line is much narrower than the absorption line, so that it can be assumed that only the peak absorption coefficient is measured. However, in the present case the only contribution to the line width (the natural line width is far too small to be of significance) in either emission from the source or absorption by the flame is the Doppler broadening. Both experiment (see below) and rough calculations show that for not too strong absorption, the assumption that it is the peak absorption coefficient that is measured can still be made provided that the emitting gas is at approximately room temperature and that the absorption is not too strong. This assumption has been made in this work.

As has been mentioned, the $f$ numbers for several of the lines have been measured. It should be pointed out, however, that the $f$ number of OH is a function of its heat of formation since in the $f$ number experiment its concentration was calculated from its thermodynamic properties[9, 10]. In our work the heat of formation of OH has been taken as 10 kcal per mole and the tabulations of B. LEWIS and G. VON ELBE[14] used to calculate equili-

brium OH concentrations. Other heats of formation have been reported[15, 16], adoption of which would of course change the measured OH concentrations reported, and more important would change the temperature dependence of various equilibrium constants to be considered. The results reported are thus uncertain due to this fact alone to a degree corresponding to the uncertainty in the heat of formation of OH.

From previous work[7, 9, 10] it can be shown that for those lines for which $f$ numbers (corrected) were measured

$$f_i = 3{\cdot}07 \times 10^{-4}\ A_K/(2J+1) \qquad \ldots\ [1]$$

where $A_K$ is the relative transition probability tabulated for all of the lines by G. H. DIEKE and H. M. CROSSWHITE, and $J$ is the rotational quantum number in the lower, $^2\Pi$, state, both for the level $i$. From the definition of the $f$ number it follows that

$$[\mathrm{OH}]_i = \frac{mc^2}{\pi e^2}\,\frac{(2J+1)}{A_K}\int \alpha_\nu \mathrm{d}\nu \times 3{\cdot}25 \times 10^{3} \qquad \ldots\ [2]$$

where $[\mathrm{OH}]_i$ is the number of molecules per cm$^3$ in the rotational level $i$, $m$ and $e$ are the mass and charge of the electron, $c$ is the velocity of light, $\alpha_\nu$ is the absorption coefficient in cm$^{-1}$ at the wave number $\nu$. The integral is taken over the whole line. For a line with a Doppler shape the integrated absorption coefficient is

$$\int \alpha_\nu \mathrm{d}\nu = 1{\cdot}065\ \alpha_0 \Delta\nu_D \qquad \ldots\ [3]$$

where $\alpha_0$ is the peak absorption coefficient at the centre of the line and $\Delta\nu_D$ is the width in cm$^{-1}$ of the line at half intensity. Combining equations 2 and 3

$$[\mathrm{OH}]_i = \frac{mc^2}{\pi e^2}\,\frac{(2J+1)}{A_K}\,\alpha_0 \Delta\nu_D \times 3{\cdot}46 \times 10^{3} \qquad \ldots\ [4]$$

If rotational equilibration exists

$$[\mathrm{OH}]_i = \{[\mathrm{OH}]/Q_{r,v}\}\,(2J+1)\exp(-E_i/RT) \qquad \ldots\ [5]$$

where [OH] is the total concentration of hydroxyl in the $^2\Pi$ state, $Q_{r,v}$ is the rotation–vibration partition function and $E_i$ is the rotational energy of the level $i$. Combining equations 4 and 5 and inserting the numerical value of the constants

$$[\mathrm{OH}] = (Q_{r,v}\alpha_0\Delta\nu_D/A_K)\exp(E_i/RT)\,3{\cdot}94 \times 10^{15} \qquad \ldots\ [6]$$

For a constant [OH], i.e. fixed positions over burner, this equation can be used to determine whether rotational equilibrium exists, and if so to determine the rotational temperature, by plotting log $(\alpha_0/A_K)_i$ against $E_i/R$. If a rotational temperature does exist as it always did in this work then equation 6 as written can be used to calculate [OH] from the results for any line. The partition functions were calculated by the equation[17]

$$Q_{r,v} = (kT/hcB)\sum_n \exp(-E_n/kT) \qquad \ldots\ [7]$$

where $k$ is the Boltzmann constant, $h$ is Planck's constant, $B$ is the rotational constant for OH taken as 18·51 cm$^{-1}$, and the $E_n$ are the energies

of the vibrational levels $n$. Actual summation over the rotational levels at one temperature showed this expression to be sufficiently accurate.

## EXPERIMENTAL

The experimental arrangement is indicated in *Figure 1*. Light from a discharge through a horizontal capillary was focused over the burner by the long focal length mirror $M_1$ (radius of curvature 60 in., diameter 4 in.). This light was gathered by another mirror $M_2$ (32 in. r.c.) and focused on the slit of the monochromator. The average thickness of the beam as it passed over the burner [*Figure 1*(b)] was about 1·5 mm. The space resolving power in the vertical direction was about 1 mm and was actually determined by the aperture of the monochromator, as was shown by projecting a light through its entrance slit backwards through the optical path. Care was taken to ensure that the direction of the beam was parallel to the burner surface. The optical system was fixed and the burner was mounted on a manipulator to allow movement in the vertical direction. For some of the experiments in which the absorption was low, a double pass system was used. Mirror $M_2$ was rotated to return the beam across the burner close to the original beam, thus almost doubling the path length. Care was taken to ensure that the two beams passed over the burner at the same height.

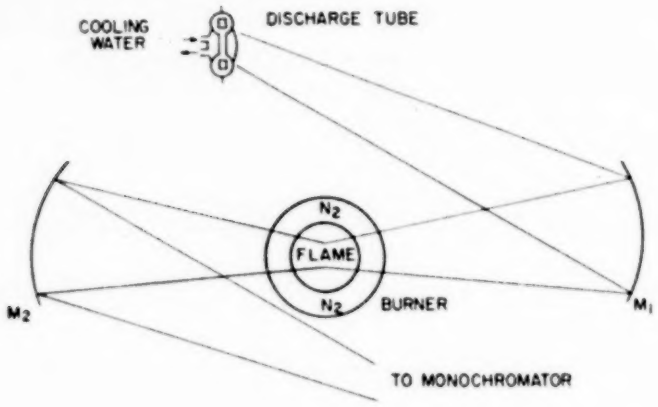


*Figure 1* (a). *Top view of experimental arrangement*

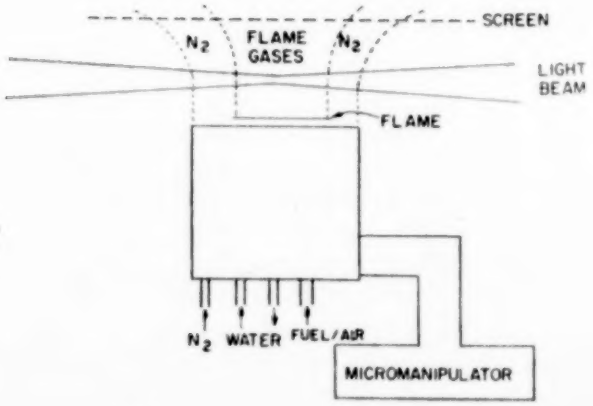


*Figure 1* (b). *Side view of burner showing flow lines and probing light beam*

For experiments at less than one atmosphere the apparatus sketched in *Figure 2* was used. This consisted of a porous burner soldered to a brass baseplate on which a bell jar rested. The vacuum seal between the bell jar and baseplate was effected by simply letting the bell jar rest on a silicone gasket, the force due to the pressure difference being sufficient to prevent leakage. The thermocouple and screen were both held on shafts brought through the baseplate by means of O-ring seals. The shafts were capable of rotation and vertical movement. The quartz windows were waxed on to side arms in the bell jar. At low pressures ignition was easily accomplished by first igniting a small hydrogen jet in the air stream with a Tesla coil, and then turning on the fuel flow. The entire apparatus rested on sets of shims, and the beam to burner distance was changed by discrete amounts by changing the shims.

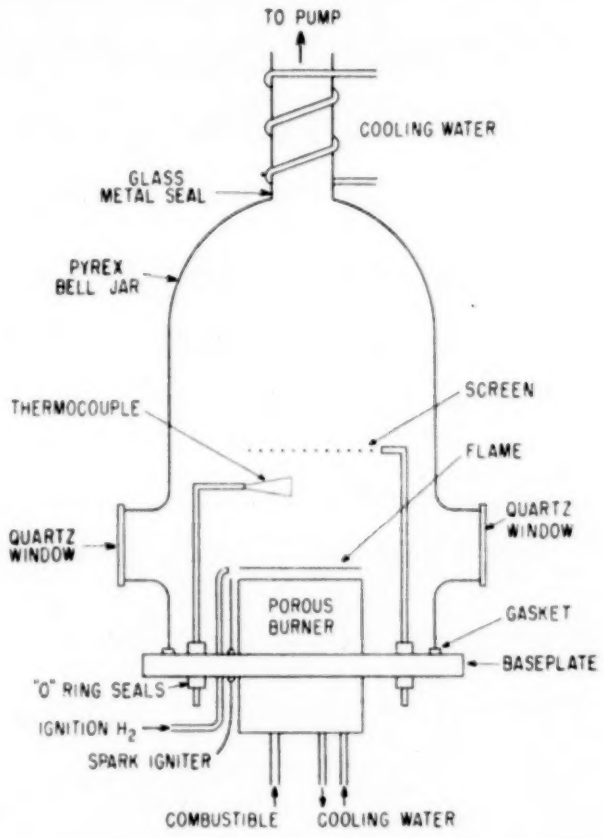


*Figure 2. Low pressure burner*

The light source was a d.c. discharge in water vapour flowing through a water-cooled quartz capillary of approximately 1 mm diameter. The pressure of water vapour was not measured but it was probably a few millimetres of mercury. The discharge current was generally 30 mA but it was shown that under a given set of conditions the absorption of an OH line was independent of current up to 100 mA. This suggests that

the cooling was effective and supports the assumption of room temperature Doppler broadening.

In measuring OH in rich flames the diffusion flame between the hot products and the surrounding air (i.e. outer cone) must be eliminated. This was accomplished in the present work by using burners with an outer annulus through which nitrogen was passed to prevent contact between air and the flame gases. The nitrogen flow was not metered but was adjusted until the diffusion flame disappeared.

If the hot gases from the flame are unconfined they are of course accelerated upward by the dense surrounding air, and the envelope of the hot gases is roughly a cone. To avoid this effect a screen was placed in the path of the hot gases as shown in *Figure 1*(b). The screens counteracted the buoyant effect so that the envelope of the hot gases was roughly cylindrical in the region where measurements were made. The screens were from 15 to 30 mm from the burner, depending on what was necessary to obtain a good geometry, and care was taken to avoid making measurements too close to the screen. Use of a screen has the added advantage that with it the tendency of the hot gas column to 'flicker' is greatly reduced. Visual observation of dust particle tracks in the flow showed that the screen did not disturb the flow in the hot gas in the region where measurements were made.

The flames used in this work are quite thin so that at about 1 mm from the burner most of the temperature rise has occurred. The temperatures quoted in this paper are the maximum temperatures, generally measured with silica-coated Pt/Pt–10% Rh, 0·001 in. overall diameter thermocouples[4], and were generally from 2 to 5 mm from the burner at 1 atmosphere and as far out as 10 mm at 0·5 atmosphere. However, the final rise to maximum temperature is quite slow so that in general the region from 1 mm from the burner to 10 to 15 mm from the burner comprised a region where the temperature did not vary more than 10 to 30°C. All measurements were made in this region. There is another temperature variation due to the fact that the porous metal is not uniform so that the gas velocity actually varies over the burner surface in an irregular manner. In the burners used here, these variations are smooth and the distances from one peak to another were of the order of a centimetre. The variation in the maximum temperature measured along the optical path was generally of the order of 50°C. Temperature measurements made by thermocouples were made at a position giving approximately the average temperature.

A 50 cm Ebert-mounting grating monochromator* was used with photoelectric recording to make the absorption measurements. The grating had 1 200 lines per mm and a ruled area of 52 mm × 52 mm. With straight 10 micron slits masked down to a length of about 1 cm the actual resolving power in the second order was at least 0·12 Å, as determined by the separation of pairs of lines in the OH spectrum. The wavelength list of Dieke and Crosswhite[7] was used to select about 20 of the stronger lines which should have been completely resolved with this resolving power.

*Manufactured by the Jarrell-Ash Company.

For many of the flames a check for rotational equilibration was made by measuring the absorption of several lines and plotting log $z_0/A_K$ against $E/R$ (equation 6). Except for very strong absorption these plots were straight lines within experimental error, and the temperatures derived from these agreed with the thermocouple temperatures (corrected for radiation loss[4]) within 50°C, the latter generally being higher. Hence for most of the runs measurements were made for only one line, $P_1 5$ or $Q_2 8$, and the temperature obtained by thermocouple, since this was easier and more precise.

For strong absorption (i.e. 80 to 90% absorption for the strongest lines) a small but reproducible curvature in the temperature plot was obtained. An example is shown in *Figure 3*, in which the estimated experimental error in log $z_0/A_K$ is indicated by the height of the data point. No straight line can be made to pass through all the points. The points for the strong lines fell lower on the average than the rest. It is felt that this small but reproducible effect is not an anomaly but simply a reflection of the fact

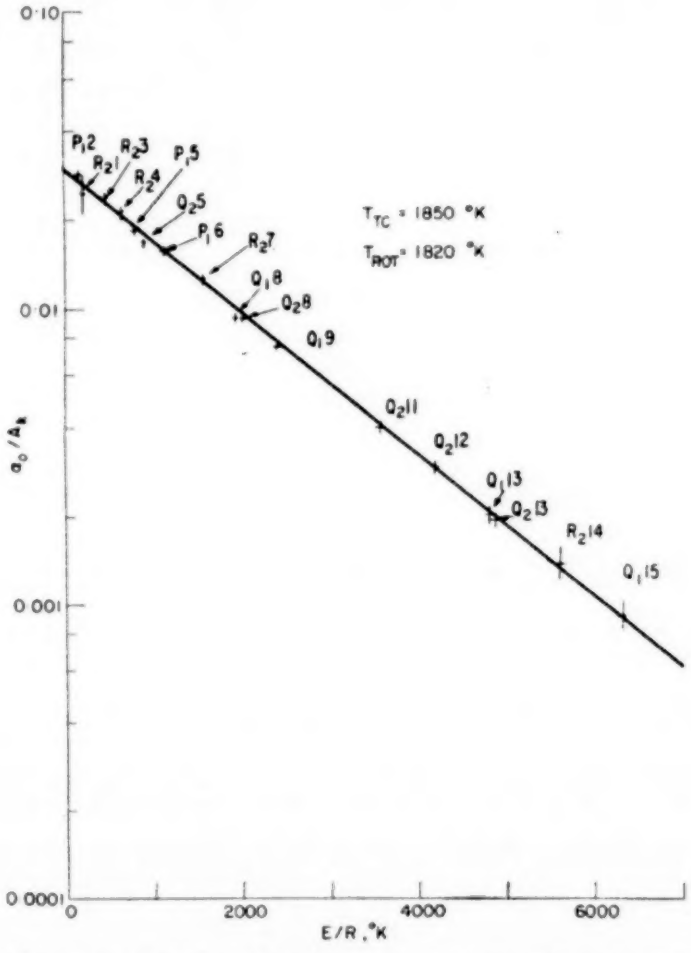


*Figure 3. Rotational temperature plot (equation 6). The temperatures derived from the line in the figure ($T_{rot.}$) and that determined by a silica-coated thermocouple ($T_{tc}$) are shown*

that the emitted line has a finite width and because of this at high absorption the measured absorption coefficient falls too low. Rough calculations assuming Doppler widths characteristic of 300°K and 1 800°K indicate a deviation of about the amount shown in the figure.

## RESULTS

Invariably it was found that the OH concentrations measured near the flame (1 to 2 mm away) were in excess of equilibrium. The variation in the observed maximum concentrations, about 30-fold from the lowest to the highest, was over a much smaller range than the variation in the ratio of the observed to the equilibrium concentrations. The latter ratios were often higher than one thousand in agreement with other observations[2, 5]. The concentrations to be expected in the reaction zones of the flames would be still higher.

Some representative data are shown in *Table 1*. The second column shows the volume fuel/air ratio and the third unburnt gas velocity measured at 25° C and the pressure of the experiment. The temperature and pressure are given in the next two columns. The length of the optical path is given in column 6. The 7th and 8th columns show the maximum and minimum OH concentrations observed in the particular run, and column 9 gives the ratio of the observed maximum OH concentration to equilibrium concentration as calculated from the data given by Lewis and von Elbe[14]. Column 10 gives the distance from the burner at which $[OH]_{max}$ was measured. Column 11 gives the ratio of [H] to [OH] at equilibrium. The last two columns will be discussed later.

In all cases the initially high OH concentrations were observed to decay toward but not to the calculated equilibrium concentrations. In a few of the runs with low OH concentrations the data were not sufficient to determine the order of the decay but in most of the runs the decay was clearly second order in OH. A few representative 1/[OH]–time plots are shown in *Figure 4*. For these the time scale is derived from the distance scale, the cold gas velocity, the expansion due to temperature rise, and the mole change due to reaction. Time zero is taken at the burner surface assuming uniform velocity. It should be pointed out that whereas the differences in distance between data points were measured to within 0·2 mm, the position of the burner surface is several times more uncertain.

Apart from uncertainties in the thermodynamics of OH, there are here three principal errors in the OH determination. The first, arising from lack of precise knowledge of line shapes, has already been discussed and is most important at high absorption. The second arose in measuring intensities and was governed by the noise in the system. The noise levels were generally from one to five per cent of the signal, but it is felt that the averaging times were sufficient to allow intensity measurements to one per cent. Data were not generally taken when the absorption was less than about 10 per cent, corresponding to an uncertainty in concentration of about 20 per cent. However, for very rich flames (runs 60 and 61) the absorption was less and the errors correspondingly greater. The third

*Table 1*

| *Run* | *Hydrogen / Air* | $v_{25}$ *cm/sec* | $T_{gas}$ °K | *P atm* | *L cm* | $[OH]_{max.}$ $[OH]_{min.}$ $10^{-16}$ *molecules/cm³* | | $\frac{[OH]_{max.}}{[OH]_{eqn.}}$ | $z_{min.}$ *mm* | $\frac{[H]}{[OH]}$ | $k_s M \times 10^{13}$ *cm³/molecule sec* | *Correction %* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 19 | 0·430 | 32·2 | 1690 | 1·0 | 4·7 | 0·37 | 0·12 | 43 | 3·0 | 0·7 | 0·6 | |
| 17 | 0·445 | 20·6 | 1550 | 1·0 | 4·7 | 0·24 | 0·037 | 260 | 1·5 | 2·5 | 0·55 | |
| 63 | 0·445 | 39·6 | 1620 | 0·5 | 7·5 | 0·328 | 0·13 | 220 | 3·5 | 2·32 | 0·2 | |
| 16 | 0·445 | 39·7 | 1760 | 1·0 | 4·7 | 0·567 | 0·065 | 48 | 1·5 | 1·34 | 0·55 | |
| 31 | 0·471 | 13·3 | 1360 | 1·0 | 9·0 | 0·065 | 0·010 | 2000 | 1·5 | 9·4 | 0·3 | |
| 26 | 0·471 | 33·1 | 1615 | 1·0 | 9·0 | 0·148 | 0·027 | 96 | 2·5 | 3·8 | 0·5 | |
| 30 | 0·494 | 13·5 | 1320 | 1·0 | 9·0 | 0·054 | 0·008 | 4300 | 1·5 | 16·3 | 0·3 | 50–100 |
| 62 | 0·500 | 41·0 | 1550 | 0·5 | 7·5 | 0·228 | 0·037 | 800 | 2·0 | 7·4 | 0·17 | 30–40 |
| 15 | 0·500 | 43·2 | 1560 | 1·0 | 4·7 | 0·179 | 0·05 | 310 | 1·5 | 6·7 | 0·5 | |
| 28 | 0·545 | 34·7 | 1490 | 1·0 | 9·0 | 0·084 | 0·011 | 860 | 2·5 | 13·2 | 0·4 | |
| 61 | 0·67 | 30·5 | 1360 | 1·0 | 5·6 | 0·021 | 0·005 | 1450 | 3·0 | 44·0 | 0·12 | |
| 64 | 0·73 | 58·0 | 1365 | 0·5 | 7·5 | 0·060 | 0·03 | 5400 | 3·5 | 54·0 | 0·06 | 20 |
| 60 | 1·00 | 40·7 | 1430 | 1·0 | 5·6 | 0·017 | 0·004 | 610 | 3·0 | 78·0 | 0·2 | |

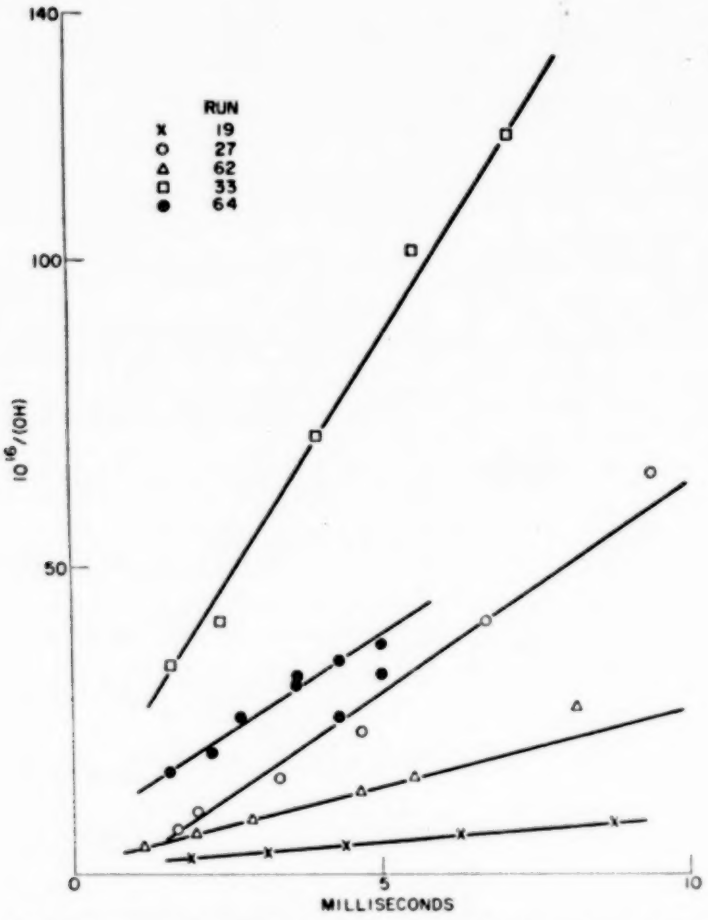


*Figure 4. Representative plots of 1/[OH] against time. The conditions of the individual runs are given in Table 1*

source of error lies in the fact that the probed region was about 1 mm thick, corresponding to a time of from 0·5 to 1 millisecond. This is 5 to 10 times larger than the error in the relative burner position. Except for the region very close to the burner, the decay curves were sufficiently straight so that the averaging over the 1 mm beam thickness should have resulted in very nearly the concentration in the centre of the beam.

Another source of error which might be expected is an edge effect, due to the mixing of the burnt gases with the surrounding cold gases. However, the agreement between runs made with burners of different diameters indicates that this was not a serious error.

## DISCUSSION

In agreement with previous work[5, 6], radical concentrations near the flame have been found to be greatly in excess of the equilibrium values. The factor by which the equilibrium value is exceeded increases markedly as the temperature is lowered. It is interesting to note that this increase is almost entirely due to the decrease in the equilibrium concentration with decreasing temperature. As will be pointed out later, the data are

consistent with a mechanism which maintains a constant [H]/[OH] ratio in the hot gases. Thus $[H]_{max.}$ is given by the product of $[OH]_{max.}$ and [H]/[OH], columns 7 and 11 in *Table 1*. The data in *Table 1* show that all the [H] calculated in this way lie within an order of magnitude of each other, but the $[OH]_{max.}/[OH]_{equ.}$, and therefore $[H]_{max.}/[H]_{equ.}$, vary by more than a factor of 100. Fenimore and Jones[5] have shown that this is to be expected on the basis of the accepted scheme for the $H_2$–$O_2$ reaction.

It should be emphasized that it is difficult to define the reaction zone of the flame and therefore to extrapolate our data to determine the maximum radical concentration in the reaction zone. This difficulty is further increased by the relatively poor accuracy in determining the beam–burner distance. It is probably generally true, however, that most of the temperature rise in the flame took place in the first millimetre or less from the burner surface.

The fact of the excess radical concentrations allows the study of processes by which complete equilibrium is approached. Bulewicz, James and Sugden[6] have pointed out that the rates of decay of the various radical concentrations in the burnt gases are not independent of each other. The following is a summary of their argument.

It is considered that there are only six chemical species of importance; the reactants $H_2$ and $O_2$, the product $H_2O$, and the three radicals OH, H and O. $N_2$ is merely a diluent and $H_2O_2$ and $HO_2$ are considered unimportant because of their presumed high temperature instability and consequent low concentrations. The fastest reactions between these six species will presumably be bimolecular reactions and if one considers only these six species, all of the possible bimolecular reactions (except exchange reactions) and their reverses can be written:

$$OH + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O + H \qquad \ldots . \ [8]$$

$$H + O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} OH + O \qquad \ldots . \ [9]$$

$$O + H_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} OH + H \qquad \ldots . \ [10]$$

$$OH + OH \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} H_2 + O_2 \qquad \ldots . \ [11]$$

$$OH + OH \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} H_2O + O \qquad \ldots . \ [12]$$

$$H_2 + O_2 \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} H_2O + O \qquad \ldots . \ [13]$$

It can be seen by inspection that considering only these 12 reactions it is possible to define a function of the concentrations of the free radicals and the deficient component, $O_2$, whose time derivative is zero. This is

$$F_R = [H] + [OH] + 2[O] + 2[O_2] \quad \ldots . \quad [14]$$

Thus these six reactions and their reverses alone cannot bring about equilibrium, but instead would lead to the establishment of a steady state in which the various radical concentrations are related to each other in the same way as at equilibrium. In this steady state either all of the radicals are at equilibrium or they all are not; and if they are not, they are all either above or below their equilibrium concentrations. This function can actually be derived from only the first three of the six reversible reactions. Addition of the last three changes neither the steady state reached nor the behaviour of the function.

The only way in which equilibrium can be reached is to introduce radical recombination reactions. These presumably will be three body reactions and relatively slow. Those which might be expected *a priori* to be significant are:

$$H + OH + M \xrightarrow{k_7} H_2O + M \quad \ldots . \quad [15]$$

$$H + H + M \xrightarrow{k_8} H_2 + M \quad \ldots . \quad [16]$$

$$O + O + M \xrightarrow{k_9} O_2 + M \quad \ldots . \quad [17]$$

The situation with which we are concerned is that of considerably higher than equilibrium concentrations so that the reverses of these reactions will not be considered. Since the function defined above cannot change due to reactions 8 to 13 and their reverses, it can only change due to reactions 15 to 17. Thus we can write for rich flames

$$d[H + OH + 2O + 2O_2]/dt = 2k_7 M [H][OH] + 2k_8 M [H]^2 + 4k_9 M [O]^2 \quad \ldots . \quad [18]$$

*Table 2*

| *Run* | [H]/[OH] | $10^{-16} \times$ *molecules/cm*$^3$ | | |
|---|---|---|---|---|
| | | $[OH]_{max.}$ | $[O_2]_{max.}$ | $[O]_{max.}$ |
| 19 | 0·7 | 0·37 | 0·34 | 0·025 |
| 17 | 2·5 | 0·24 | 0·097 | 0·015 |
| 16 | 1·45 | 0·567 | 0·29 | 0·048 |
| 31 | 9·4 | 0·065 | 0·008 | 0·0033 |
| 26 | 3·8 | 0·148 | 0·016 | 0·0049 |
| 30 | 16·3 | 0·054 | 0·0046 | 0·0021 |
| 15 | 6·7 | 0·179 | 0·0185 | 0·0085 |

If only reactions 8 to 10 were operative, the following relationships between the concentrations of radicals and oxygen would eventually be established:

$$[H] = K_1 \frac{[H_2]}{[H_2O]} [OH] \quad \ldots\ldots [19]$$

$$O = \frac{K_1 [OH]^2}{K_3 \cdot [H_2O]} \quad \ldots\ldots [20]$$

$$O_2 = \frac{[OH]^2}{K_2 K_3 [H_2]} \quad \ldots\ldots [21]$$

where the $K$s are the equilibrium constants. If reactions 8 to 10 are rapid compared with 15 to 17, then equations 19 to 21 would be expected to apply to an approximation depending on the relative speed of the two sets of reactions. In the event that the first set is sufficiently rapid then all of the concentrations in equation 18 can be expressed in terms of OH and the equation integrated to give an expression for the decay.

In interpreting the data reported here, the first thing that can be asked is whether all of the radicals and oxygen are to be expected to be present in sufficient quantity to contribute to the function $F_H$. In *Table 2* are some representative values for [OH], [O], [$O_2$] and the [H]/[OH] ratio calculated from the experimental [OH] and equations 19 to 21. These are the maximum values for the particular run. As the gases pass downstream the [H]/[OH] ratio will remain constant, but [O] and [$O_2$] will drop off more rapidly than [OH] since they are proportional to [OH]$^2$. From *Table 2* it can be seen that the O concentrations are always too low to contribute, and except for the most nearly stoichiometric runs the same is true of $O_2$. Thus it will be assumed that only OH and H and reaction 8 are significant.

Next it can be asked whether reaction 8 is expected to be rapid enough to allow equilibration in the times allowed. A value for $k_1$ has been published by L. AVRAMENKO and R. LORENTSO[15], and approximately verified at flame temperatures by C. P. FENIMORE and G. W. JONES[5]. Using this value of $7 \times 10^{-12} (T)^{1/2} \exp(-10\,000/RT)$ and the data in *Table 1*, it is easily shown that the products $k_1 [H_2]$ and $k_{-1} [H_2O]$ are always greater than $10^1$ sec$^{-1}$, corresponding to a lifetime of OH or H of 0·1 msec or less. On the other hand, in our experiments data points were generally from 0·5 to 1 msec apart in time. Thus the assumption that reaction 8 is equilibrated appears to be a very reasonable one to make.

On substituting equation 19 into 18, one gets

$$\left[1 + K_1 \frac{[H_2]}{[H_2O]}\right] \frac{d}{dt} [OH] = 2K_1 \frac{[H_2]}{[H_2O]} [OH]^2 k_7 M + 2 \left[K_1 \frac{[H_2]}{[H_2O]}\right]^2 [OH]^2 k_8 M \quad \ldots\ldots [22]$$

and on integrating, with the further assumption that $k_7 = k_8$,

$$\frac{1}{[OH]} = 2K_1 \frac{[H_2]}{[H_2O]} k_8 M t + \text{a constant} \quad \ldots\ldots [23]$$

This last assumption is a simplifying and not a necessary assumption and will be reconsidered in the light of the experimental results.

Equation 23 predicts a second order decay in OH as was observed. The values of $k_8$M calculated from equation 23 are given in column 12 of *Table 1*. For these $[H_2]$ and $[H_2O]$ were calculated assuming the stoichiometric formation of water. $K_1$ was obtained from the data given by Lewis and von Elbe[14]. There is a definite variation of $k_8$M with composition, as well as an apparent dependence on flame speed (temperature). The predicted pressure effect on $k_8$M is shown by comparison of pairs of runs of about the same composition and temperature but different pressure.

The question immediately arises as to whether diffusion can account for any of the variation observed. Assuming that the picture presented here is qualitatively correct, it is principally the decay of H atoms due to reaction 16 which is being observed. The differential equation including diffusion for the variation of [H] with $z$, the normal to the flame surface, is

$$D\frac{d^2[H]}{dz^2} - V\frac{d[H]}{dz} - 2k'_8[H]^2 = 0 \qquad \ldots\ [24]$$

where $D$ is the coefficient of diffusion of H in the hot gas, $V$ is the hot gas velocity and $k'_8$ is the actual reaction rate constant. The rate constants in *Table 1* have been derived assuming the first term on the left is always zero. We have been unable to obtain an analytical solution to this equation. The effect of diffusion can be approximated by computing the numerical values of the first two terms at various distances. This has been done for three runs taking a constant diffusion coefficient for H into the rest of the mixture, using a collision cross section of 3 Å. The magnitudes of the corrections to be added to $k_8$M are shown in the last column of *Table 1*. The expected corrections are seen to be quite appreciable for the slow flames and moderate for the faster. It appears that diffusion can account for the low values of $k_8$M obtained from the slower flames, but probably cannot explain the variation with composition.

The most reasonable explanation for this effect of composition would seem to be that actually $k_7$ is larger than $k_8$. It is difficult to make this statement more quantitative for two reasons. The first is the fact that the gas metering error of about 0·5 per cent in each gas makes the composition of the nearly stoichiometric flames somewhat uncertain. The other lies in the fact that any effects due to $O_2$ have been neglected. Inclusion of a term in $O_2$ in equation 17 would not have led to a simple second order decay. If this effect were present but not noticeable the result would have been a tendency for the rate constant to be too low, since $O_2$ would contribute to the pool of radicals without providing an additional means for disappearance. One can only say that $k_7$ is probably larger than $k_8$, but of the same magnitude.

For the richest flames where the [H]/[OH] ratio is large, there is little doubt that what is being observed is only the recombination of H atoms. The average value of $k_8$M of about $0{\cdot}3 \times 10^{-13}$ cm$^3$/mole sec compares

favourably with the value of $0{\cdot}2 \times 10^{-13}$ cm$^3$/mole sec found in richer flames by a different method[6].

*The author wishes to thank Drs C. P. Fenimore and G. E. Moore for many helpful discussions, and Mr W. W. Crotty who made many of the measurements.*

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*(Received April 1958)*

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# The Spontaneous Ignition of Alkyl Silanes

S. T. GRIFFITHS and R. R. WILSON

*The spontaneous ignition temperatures of a number of alkyl silanes have been determined and compared with the chemical structures of these compounds. A 'drop' technique, based on the method described by Wiezevich* et al., *was used. Because of the need for standardization of the experimental procedure in this type of method, the spontaneous ignition temperatures were determined at a fixed delay time of five seconds, and with a fuel/air ratio controlled between the limits of two and three times the stoichiometric requirement. With these conditions, the repeatability of the results was, in general, good. These results permit a qualitative discussion of the possible influence of silicon–hydrogen bonds on the ease of oxidation as indicated by differences in the spontaneous ignition temperatures. Thus with the ethyl silanes the ease of oxidation decreases in the order*

$$Et_2SiH_2 > Et_3SiH > Et_4Si$$

*The same order was found by Schalla* et al. *for the methyl silane series.*

*The differences in spontaneous ignition temperatures are less pronounced in the* n-*propyl series, and still less pronounced in the* n-*butyl series and in the* n-*amyl series. These results suggest that the silicon–hydrogen bonds have less influence on the ease of oxidation in the higher homologues. The relative effect of primary, secondary and tertiary silicon–hydrogen bonds is shown by comparing the ease of oxidation in a series of silanes containing 5 carbon atoms* (n-*amyl,* n-*propyl ethyl, di-ethyl methyl silanes) and 6 carbon atoms* (n-*hexyl,* n-*butyl ethyl, di-*n-*propyl and tri-ethyl silanes). In both series the ease of oxidation decreases in the order*

*primary > secondary > tertiary*

*In isomeric dialkyl silanes, such as di-*n-*propyl and* n-*butyl ethyl silanes, the greater the symmetry of the molecule about the* $SiH_2$ *group, the more resistant it is to oxidation.*

DURING the past fifty years, many investigators have studied the effect of the molecular structure of hydrocarbons upon spontaneous ignition temperature. An excellent review of the various methods employed in determining the spontaneous ignition temperature of liquid fuels, has been presented by B. P. MULLINS[1]. Each method has advantages and disadvantages, but the 'static' method, using the 'drop' technique, is highly commendable by virtue of its simplicity. From time to time, criticism has been directed at this method, chiefly on account of lack of standardization of both the apparatus and test procedure, and it is well known that the spontaneous ignition temperature of a given hydrocarbon is dependent upon these two factors. Within a given apparatus, and employing a standard test procedure, this technique affords the great advantage of permitting a large number of repeatable determinations to be made in a short space of time.

The present study concerns the determination of spontaneous ignition temperatures of a number of *n*-alkyl silanes, using the 'drop' technique based upon a method already described[2]. The *n*-alkyl silane compounds were so chosen as to permit general considerations of the effect of molecular structure upon spontaneous ignition temperature. Further, the spontaneous

ignition temperatures of these compounds would appear to indicate their relative ease of oxidation, and this view is in accord with the correlation that exists between these properties for hydrocarbons[3].

## EXPERIMENTAL

### *Materials*

The organo-silicon compounds used in this investigation were prepared in one of the following ways:

The tetra-alkyl silanes, by reaction with either the appropriate Grignard reagent or lithium alkyl upon silicon tetrachloride

The tri-alkyl silanes, by reaction of the appropriate lithium alkyl upon silico-chloroform

The mono-alkyl and di-alkyl silanes, by reduction of the corresponding di- and tri-chlorides by treatment with lithium aluminium hydride in either anhydrous diethyl ether or dioxan solution[4].

All the compounds were distilled in a small packed column, and boiling point data are given in *Table 1*.

*Table 1. Boiling points of* n*-alkyl silanes*

| *Compound* | *B.pt* °*C* | *mm* Hg | *Compound* | *B.pt* °*C* | *mm* Hg |
|---|---|---|---|---|---|
| Methyl silane series | | | Butyl silane series (*continued*) | | |
| *Tetra-methyl* | 26·2 | 760 | *Di-butyl* | 159·0–160·0 | 761 |
| *Tri-methyl* | 6·7 | 760 | *Mono-butyl* | 55·0– 56·5 | 751 |
| *Di-methyl* | −19·6 | 760 | | | |
| *Mono-methyl* | −57·5 | 760 | Amyl silane series | | |
| | | | *Tetra-amyl* | 310·0–320·0 | 750 |
| Ethyl silane series | | | *Tri-amyl* | 129·0 | 4 |
| *Tetra-ethyl* | 153·0–155·0 | 750 | *Di-amyl* | 189·0–190·0 | 755 |
| *Tri-ethyl* | 108·0–109·0 | 754 | *Mono-amyl* | 85·5– 86·5 | 754 |
| *Di-ethyl* | 54·0– 56·0 | 751 | | | |
| | | | Hexyl silane series | | |
| | | | *Mono-hexyl* | 116·0–117·0 | 754 |
| Propyl silane series | | | | | |
| *Tetra-propyl* | 215·0–218·0 | 751 | 5-Carbon atom silane series | | |
| *Tri-propyl* | 170·0–171·0 | 756 | *Propyl ethyl* | 88·0– 90·0 | 749 |
| *Di-propyl* | 110·0–113·0 | 755 | *Butyl methyl* | 81·0– 83·0 | 753 |
| *Mono-propyl* | 22·0– 25·0 | 749 | *Di-ethyl methyl* | 75·0– 77·0 | 757 |
| | | | | | |
| Butyl silane series | | | 6-Carbon atom silane series | | |
| *Tetra-butyl* | 270·0 | 749 | | | |
| *Tri-butyl* | 225·0–226·0 | 755 | *Mono-butyl ethyl* | 115·0–118·0 | 747 |

The normal paraffins employed were obtained as follows:

pentane and *n*-hexane, from May & Baker Ltd
heptane, from Phillips Petroleum Co. Ltd
octane and undecane, from L. Light & Co. Ltd

*Apparatus*

The ignition apparatus (*Figure 1*) was similar to that described by P. G. WIEZEVICH *et al.*[2], except that the metal block was electrically heated by ten 300W strip heaters mounted round the periphery and connected in parallel to a 110V a.c. supply. The temperature was measured with a chromel/alumel thermocouple, cold junction compensated, used with a direct reading instrument. The thermocouple and pyrometer had been previously calibrated at 320·9°C, using the freezing point of cadmium of assay quality as reference.

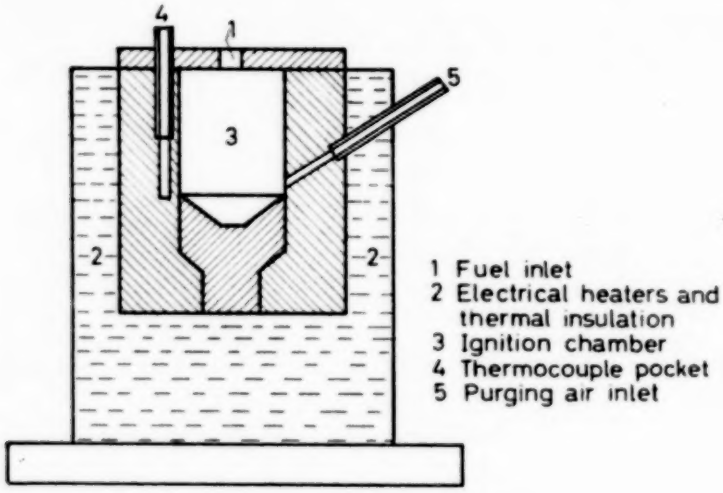


*Figure 1. Spontaneous ignition apparatus*

*Test procedure*

The determination of spontaneous ignition temperature was carried out by heating the apparatus up to 50° to 70°C above the expected ignition temperature. A drop of the compound under examination was allowed to fall into the ignition chamber, and the time to spontaneous ignition was measured using a stopwatch graduated to 0·2 second. The chamber was purged with compressed air and the procedure was repeated as the ignition apparatus cooled, to obtain the relationship between ignition delay and ignition temperature. Several sets of data were obtained for each compound, and from these results a value of the spontaneous ignition temperature at a standard delay time of five seconds was obtained.

An interval of five seconds was chosen because it was less than the maximum delay for any of the compounds examined, and was considered adequate time for the droplet vapours to mix with the air in the ignition chamber.

By suitable choice of small glass syringes, it was possible to control the fuel/air ratio of the compounds examined, between the limits of two and three times the stoichiometric requirement. Under these conditions, the repeatability of the results was in all cases ±5°C, and usually better than this.

## RESULTS

The spontaneous ignition temperatures of the *n*-alkyl silanes studied are given in *Table 2*.

*Table 2. Spontaneous ignition of* n-*alkyl silanes*

| *Compound* | *Spontaneous ignition temperature at 5 seconds delay °C* | *Compound* | *Spontaneous ignition temperature at 5 seconds delay °C* |
|---|---|---|---|
| Methyl silanes | | Butyl silanes (*cont.*) | |
| *Tetra-methyl*[5] | 450 | *Di-butyl* | 245 |
| *Tri-methyl*[5] | 320 | *Mono-butyl* | 241 |
| *Di-methyl*[5] | 230 | | |
| *Mono-methyl*[5] | 130 | Amyl silanes | |
| | | *Tetra-amyl* | 260 |
| Ethyl silanes | | *Tri-amyl* | 253 |
| | | *Di-amyl* | 253 |
| *Tetra-ethyl* | 333 | *Mono-amyl* | 236 |
| *Tri-ethyl* | 296 | | |
| *Di-ethyl* | 274 | Hexyl silanes | |
| | | *Mono-hexyl silane* | 238 |
| Propyl silanes | | | |
| *Tetra-propyl* | 282 | 5-Carbon atom silanes | |
| *Tri-propyl* | 278 | *Propyl ethyl silane* | 278 |
| *Di-propyl* | 281 | *Butyl methyl silane* | 236 |
| *Mono-propyl* | 253 | *Di-ethyl methyl silane* | 307 |
| Butyl silanes | | | |
| | | 6-Carbon atom silane | |
| *Tetra-butyl* | 260 | | |
| *Tri-butyl* | 253 | *Butyl ethyl silane* | 258 |

The majority of these compounds are shown below, and have been classified according to both 'series' and 'type'.

For the purpose of discussion, the spontaneous ignition results of R. L. SCHALLA, G. E. MCDONALD and M. GERSTEIN[5] for the methyl silane series at 2·5 times the stoichiometric ratio, have been included. It should be noted that these workers determined the spontaneous ignition of these silanes in a closed reaction vessel, and the values quoted in this paper are not strictly comparable to the present results. However, qualitative comparison is considered justifiable.

| *Type* / *Series* | $RSiH_3$ | $R_2SiH_2$ | $R_3SiH$ | $R_4Si$ |
|---|---|---|---|---|
| *Methyl* | $CH_3SiH_3$ | $(CH_3)_2SiH_2$ | $(CH_3)_3SiH$ | $(CH_3)_4Si$ |
| *Ethyl* | *Not prepared* | $(C_2H_5)_2SiH_2$ | $(C_2H_5)_3SiH$ | $(C_2H_5)_4Si$ |
| *Propyl* | $(C_3H_7)SiH_3$ | $(C_3H_7)_2SiH_2$ | $(C_3H_7)_3SiH$ | $(C_3H_7)_4Si$ |
| *Butyl* | $(C_4H_9)SiH_3$ | $(C_4H_9)_2SiH_2$ | $(C_4H_9)_3SiH$ | $(C_4H_9)_4Si$ |
| *Amyl* | $(C_5H_{11})SiH_3$ | $(C_5H_{11})_2SiH_2$ | $(C_5H_{11})_3SiH$ | $(C_5H_{11})_4Si$ |
| *Hexyl* | $(C_6H_{13})SiH_3$ | | | |

Ethyl silane was not prepared on account of its low boiling point[6], 13·7°C.

In addition to the above compounds, propyl ethyl, *n*-butyl methyl, *n*-butyl ethyl and di-ethyl methyl silanes were prepared to permit considerations of the effect of symmetry of the silane molecules upon spontaneous ignition temperature.

The results for *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane and undecane were obtained using the technique already described, and are given in *Table 3*. The value for *n*-propane reported by J. L. JACKSON[7] at a delay

*Table 3. Spontaneous ignition temperatures of* n-*hydrocarbons*

| *Compound* | *Spontaneous ignition temperature at 5 seconds delay* °C | *Compound* | *Spontaneous ignition temperature at 5 seconds delay* °C |
|---|---|---|---|
| n-*Propane*[7] | 504 | n-*Heptane* | 266 |
| n-*Pentane* | 299 | n-*Octane* | 259 |
| n-*Hexane* | 285 | *Undecane* | 251 |

time of six seconds, has been included in order to indicate the higher ignition temperatures of the lower members of the *n*-paraffin series.

## DISCUSSION

### *Alkyl silane series*

From *Figure 2* it is seen that the greater the degree of alkylation of the silane, the higher is the ignition temperature, the ease of oxidation thus decreasing in the order

$$RSiH_3 > R_2SiH_2 > R_3SiH > R_4Si$$

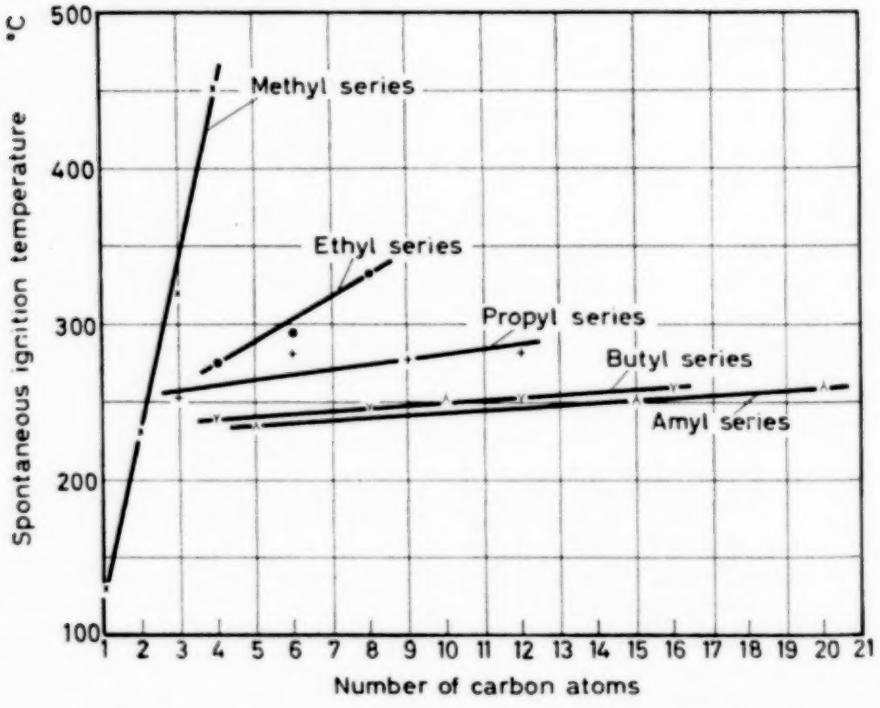


*Figure 2. Spontaneous ignition temperatures of alkyl silanes*

From being very marked in the methyl series where the ignition temperature increases from 130° for mono-methyl to 450°C for tetra-methyl silane, the effect diminishes as the alkyl group increases in size from methyl up to amyl.

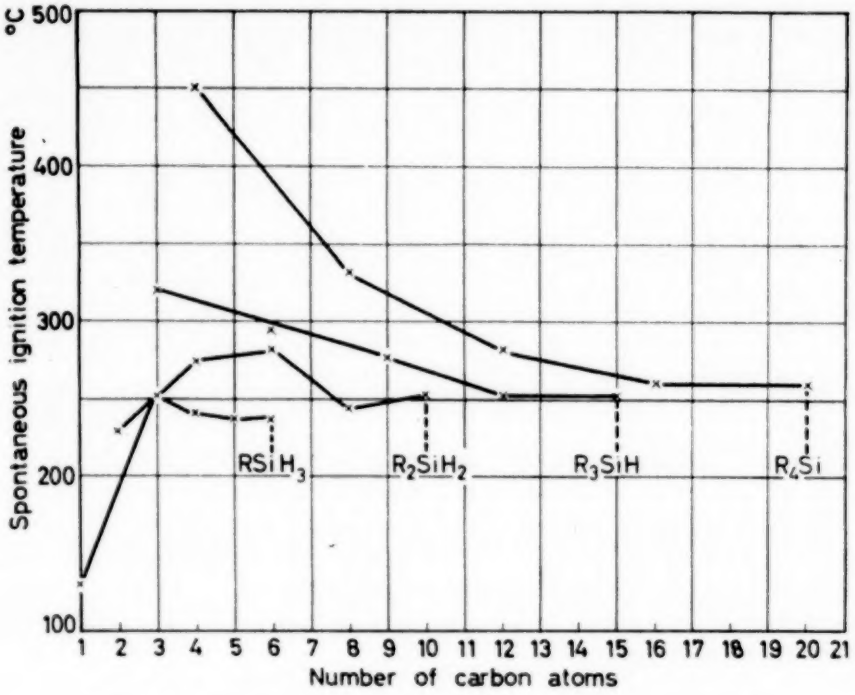


*Figure 3. Spontaneous ignition temperatures of alkyl silanes*

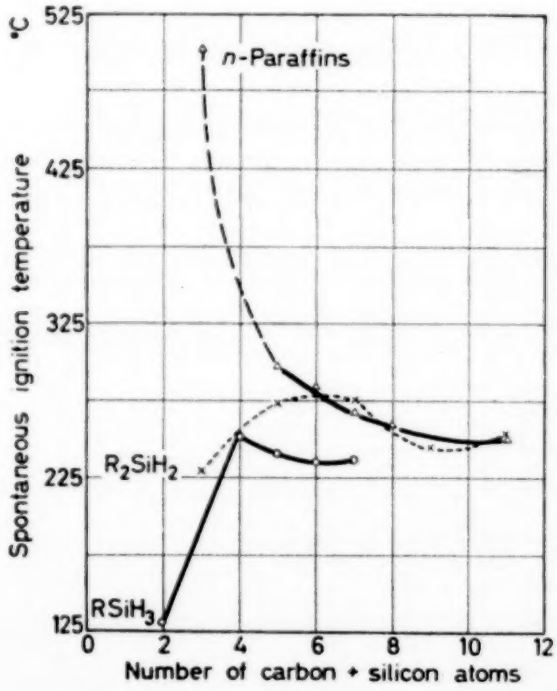


*Figure 4. Spontaneous ignition temperatures of di-alkyl silanes and mono-alkyl silanes together with corresponding n-hydrocarbon analogues*

Schalla *et al.*[5] suggest that the initial attack is at the silicon–hydrogen bond, and that the decreasing ease of oxidation in the series is due to the diminishing number of these bonds. Since this effect becomes much less marked as the hydrocarbon component increases in size, it appears that the resistance to oxidation brought about by the diminishing number of silicon–hydrogen bonds is offset in the larger molecules by an increasing ease of oxidation of the hydrocarbon component.

### $R_3SiH$ *and* $R_4Si$ *types*

In the case of the types $R_3SiH$ and $R_4Si$, the length of the *n*-alkyl side chain controls the susceptibility to spontaneous ignition in ascending the series. Tetra-*n*-amyl silane has a similar tendency to spontaneous ignition as tetra-*n*-butyl silane, indicating that the effect of the length of the alkyl side chain has achieved a limiting value. A similar argument applies to tri-*n*-amyl and tri-*n*-butyl silanes.

### $R_2SiH_2$ *type*

The results obtained for the di-alkyl silanes, $R_2SiH_2$, are of added interest, since many data are available concerning the spontaneous ignition temperatures of the corresponding hydrocarbon analogues[7]. *Figure 4* presents the results of spontaneous ignition temperatures for alkyl silanes of the type $R_2SiH_2$, and also the spontaneous ignition temperatures of the corresponding hydrocarbon analogues. The resistance of the di-alkyl silanes to spontaneous ignition reaches a maximum at di-*n*-propyl silane, the value obtained for this compound being similar to that of *n*-heptane. The molecular structures of these two compounds are:

$CH_3—CH_2—CH_2—SiH_2—CH_2—CH_2—CH_3$ di-*n*-propyl silane

$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3$ *n*-heptane

A. R. Ubbelohde[8] has found that large paraffin molecules, e.g. *n*-heptane, are 'crumpled' in the gas phase, and thus with these molecules, steric considerations may favour radical attack of primary C—H bonds. It is logical to assume that di-*n*-propyl silane undergoes a similar 'crumpling' effect, thus shielding the Si—H bonds from oxygen attack, and oxidation may proceed at the terminal primary C—H bonds, as for *n*-heptane. A similar argument may be extended to apply to di-*n*-amyl silane, and its corresponding hydrocarbon analogue undecane.

### $RSiH_3$ *type*

The *n*-paraffins are also the analogues of the mono-alkyl silane compounds, e.g. *n*-hexyl silane and *n*-heptane,

$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—SiH_3$ *n*-hexyl silane

$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3$ *n*-heptane

It is interesting to note the resistance to spontaneous ignition achieved in ascending from methyl silane to *n*-propyl silane. Further, it will be seen that maximum resistance to spontaneous ignition is displayed by *n*-propyl

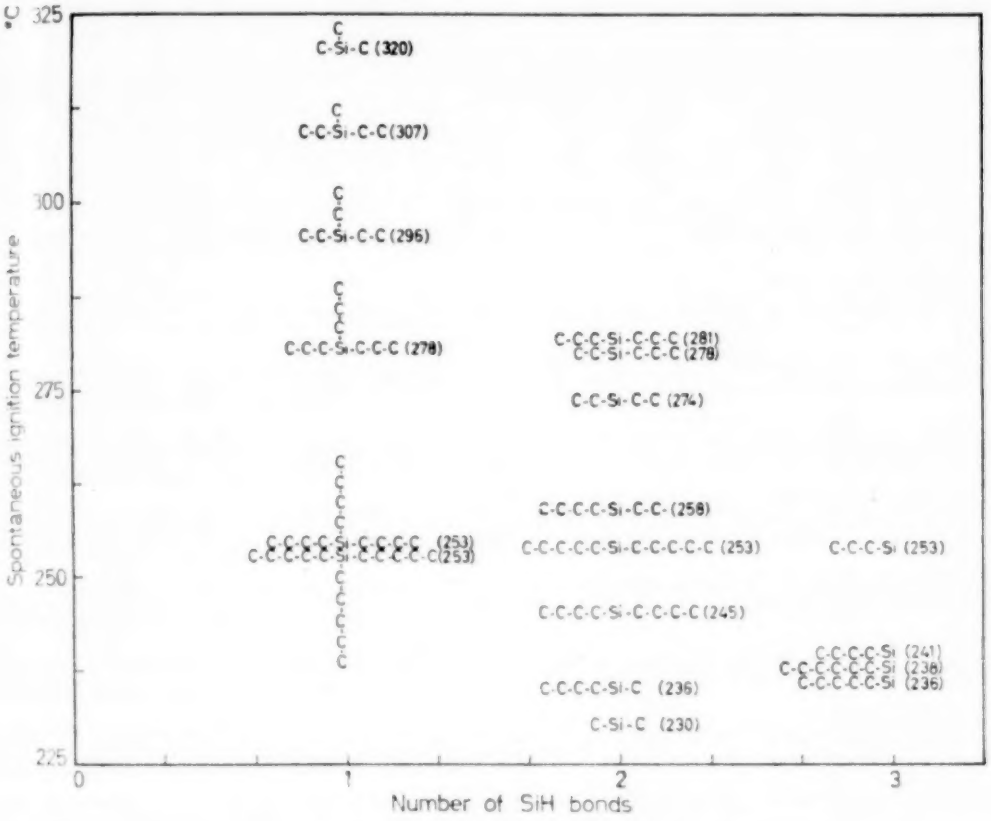


*Figure 5. Effect of molecular structure and number of* **SiH** *bonds upon spontaneous ignition temperatures of alkyl silanes*

silane, whilst maximum resistance to spontaneous ignition was achieved by di-*n*-propyl silane in the $R_2SiH_2$ type. The higher members of the type, $RSiH_3$, show a gradual increasing tendency to spontaneous ignition, which parallels the behaviour of the corresponding hydrocarbon analogues, but

| *Compound* | *Structure* | *Spontaneous ignition temp. °C* |
|---|---|---|
| 5 carbon atoms | | |
| n-*Amyl silane* | C—C—C—C—C—Si | 236 |
| n-*Butyl methyl silane* | C—C—C—C—Si—C | 236 |
| n-*Propyl ethyl silane* | C—C—C—Si—C—C | 278 |
| *Di-ethyl methyl silane* | C—C—Si—C—C<br>\|<br>C | 307 |
| 6 carbon atoms | | |
| n-*Hexyl silane* | C—C—C—C—C—C—Si | 238 |
| n-*Butyl ethyl silane* | C—C—C—C—Si—C—C | 258 |
| *Di-n-proypl silane* | C—C—C—Si—C—C—C | 281 |
| *Tri-ethyl silane* | C—C—Si—C—C<br>\|<br>C<br>\|<br>C | 296 |

at a lower spontaneous ignition temperature level, due to the presence of the terminal $SiH_3$ group.

*Isomeric silanes*

From the alkyl silanes examined, the five- and six-carbon atom isomers are worthy of individual consideration.

Three types are recognized in the table (p 251), and the general pattern of the ease of ignition already discussed in the methyl and ethyl silane series is apparent, i.e.

$$RSiH_3 > R_2SiH_2 > R_3SiH$$

*n*-Butyl methyl and *n*-propyl ethyl silanes differ only in the position of the $—SiH_2—$ group, and it is interesting to note the greater resistance to ignition afforded by the more symmetrical molecule. A similar argument may be extended to six-carbon atom isomers, *n*-butyl ethyl and di-*n*-propyl silane.

*Overall effect of* Si—H *bonds*

*Figure 5* summarizes graphically the opposing effects of a number of Si—H bonds and the carbon skeleton.

*The authors wish to acknowledge the assistance of Mr F. J. French in some of the experimental work, and also to thank The Associated Ethyl Company Limited for permission to publish this paper.*

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*(Received July 1958)*

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# The Flashback of Laminar and Turbulent Burner Flames at Reduced Pressure*

B. FINE

*The effect of reduced pressure on the critical boundary velocity gradient for flashback has been studied for laminar and turbulent burner flames of hydrogen and propane with a variety of oxygen-containing mixtures. The proportionality between the boundary velocity gradient and the burning velocity divided by the quenching distance is examined. Detailed examination is difficult because of uncertainties in pressure exponents, particularly for burning velocity. However, flame reaction orders based on flashback are in general agreement with those based on quenching and burning velocity. Comparison of flashback gradients in the turbulent and laminar regions suggests that a turbulent burner flame near flashback is stabilized in the laminar sublayer. This interpretation requires, however, that a flame in a field of pipe turbulence shall penetrate about three times closer to a cold wall than a laminar flame.*

IT HAS recently been observed[1] that the critical boundary velocity gradient for flashback of laminar flames, $g_f$, is nearly proportional to the quotient of the burning velocity divided by the quenching distance. According to K. WOHL *et al.*[2], the existence of such a relation would imply that $g_f$ is a measure of the mean flame reaction rate, and is independent of transport properties.

The present study has the following purposes: first, to check the existence of a relation between $g_f$ and experimental values of burning velocity divided by quenching distance for a few flame systems over a range of pressure; secondly, to interpret pressure exponents and constants of proportionality obtained from measurement of laminar flashback in terms of chemical reactivity; thirdly, to study the flashback of turbulent burner flames over a range of pressure. Two fuels were used, hydrogen and propane; several oxidant mixtures were used in which oxygen was the active component. Fuel–oxidant systems were chosen so that unpiloted laminar and turbulent flames flashed back over a convenient range of pressures and burner diameters. Parameters varied include pressure, fuel–oxygen ratio, diluent and burner diameter.

## EXPERIMENTAL

*Materials*—Cylinder hydrogen (98 to 99 per cent hydrogen) and propane (CP grade) were used as fuels. Cylinder compressed air, cylinder oxygen, and three prepared gas mixtures—50 per cent oxygen, 50 per cent nitrogen; 20·6 per cent oxygen, 79·4 per cent argon; and 20·6 per cent oxygen, 79·4 per cent helium—were used as oxidants. All materials were used without further purification. Henceforth, these oxidant mixtures will be referred to as 'oxygen–nitrogen', 'argon "air"', and 'helium "air"', respectively.

*NACA reference 4816.

*Apparatus*—A sketch of the apparatus, which has been described in detail elsewhere[3], is shown in *Figure 1*. The burner, which was water-jacketed near the lip, had an inside diameter of 1·89 cm and was fitted with tubular inserts 1·459, 1·016, 0·928 and 0·546 cm in diameter. Length to diameter ratios ranged from 50: 1 to 125: 1, so that fully developed laminar and turbulent pipe flow was probably assured.

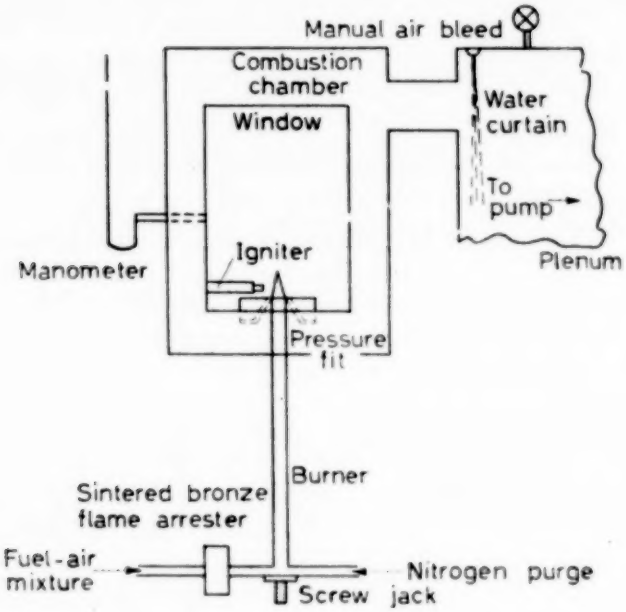


*Figure 1. Combustion apparatus*

Incoming fuel and oxidant were metered separately through calibrated critical flow orifices and then mixed. Ignition was effected at the burner port by a retractable spark igniter.

*Procedure*—Flashback was measured in a manner similar to that first reported by H. G. WOLFHARD[1]. A stable flame was established. Then the pressure was slowly increased, at constant mass flow, until the flame flashed back. The average stream velocity at which flashback occurred was computed from observation of the burner diameter, the ambient pressure and the nominal volume flow rate at 1 atmosphere pressure.

At intermediate and high Reynolds numbers, flashback was sharp and often explosive. Below a Reynolds number of about 400, however, flames did not flash back sharply, but, instead, retreated slowly into the tube. Often this movement was asymmetric, so that tilted flames were observed. In this region, the flashback pressure was chosen as the pressure at which any portion of the flame first dropped below the level of the burner rim.

In the laminar region critical boundary velocity gradients were computed by the usual relation[3]

$$g_f = 8\bar{U}_f/D \qquad \ldots\ldots[1]$$

where $\overline{U}_f$ is the mean stream velocity at flashback and $D$ is the burner diameter. In the region of fully developed turbulent flames, critical gradients were obtained by[6]

$$g_f(t) = 0{\cdot}023 \frac{R_e^{0{\cdot}8} \overline{U}_f(t)}{D} \quad \ldots . [2]$$

where the Reynolds number $R_e$ is expressed as $\overline{U}_f(t) D\rho/\eta$. The mixture density was assumed to be additive in the mole fraction. The mixture viscosity $\eta$ was computed as a function of composition by the method of L. A. BROMLEY and C. R. WILKE[7] for hydrogen-containing mixtures. For propane-containing mixtures, a simpler approximation was used

$$\eta = \sum_i [x_i \eta_i (M_i)^{1/2}] / \sum_i x_i (M_i)^{1/2} \quad \ldots . [3]$$

where $x_i$ is the mole fraction of the $i$th species, $\eta_i$ its viscosity, and $M_i$ its molar weight[8].

The range of Reynolds numbers which corresponded to a region of laminar–turbulent transition depended on the burner used. For the four largest burner sizes (1·89, 1·459, 1·016 and 0·928 cm in diameter) inlet conditions were turbulent and transition took place between Reynolds numbers of 1 500 and 2 500, independent of the fuel–oxidant mixture. For the smallest insert, 0·546 cm in diameter, inlet conditions were smoothly contoured, so that well-developed turbulent flames were not observed at Reynolds numbers below about 6 000.

In the region of laminar–turbulent transition, critical gradients were computed as for simple laminar flow (equation 1). This was felt to be justified for several reasons. First, flames in the transition region fluctuated randomly between a fully laminar and turbulent appearance; this suggested that the use of a gradient based on an interpolated friction factor, such as that used by G. L. DUGGER[9], might not be physically meaningful. Secondly, the fact that the transition region was not found in the usual range of Reynolds numbers (2 200 to 3 200) and that, moreover, its location varied with the nature of the inlet conditions suggested that no valid friction factor could be obtained based on interpolation of existing data on pipe friction. Finally, the data of the present investigation showed that the flashback pressure in the transition region was independent of pressure for any burner. This meant that the calculation of $g_f$ in a more sophisticated manner would not alter the shape of the flashback curve in the transition region, but would merely shift data points along the curve to slightly higher values of $g_f$.

## RESULTS

### *General description*

Flashback data for laminar and turbulent flames are shown plotted in *Figures 2* to *7* in the form log pressure against log $g_f$. Results are shown for hydrogen–air, hydrogen–argon 'air', and hydrogen–helium 'air' at an

equivalence ratio* of 1·50; for propane–oxygen–nitrogen and propane–argon 'air' flames at an equivalence ratio of one; and for propane–oxygen flames at an equivalence ratio of 0·85. It is seen that, for a given fuel–oxidant mixture, there are two ranges of data over which the critical flashback gradient is independent of burner diameter and over which

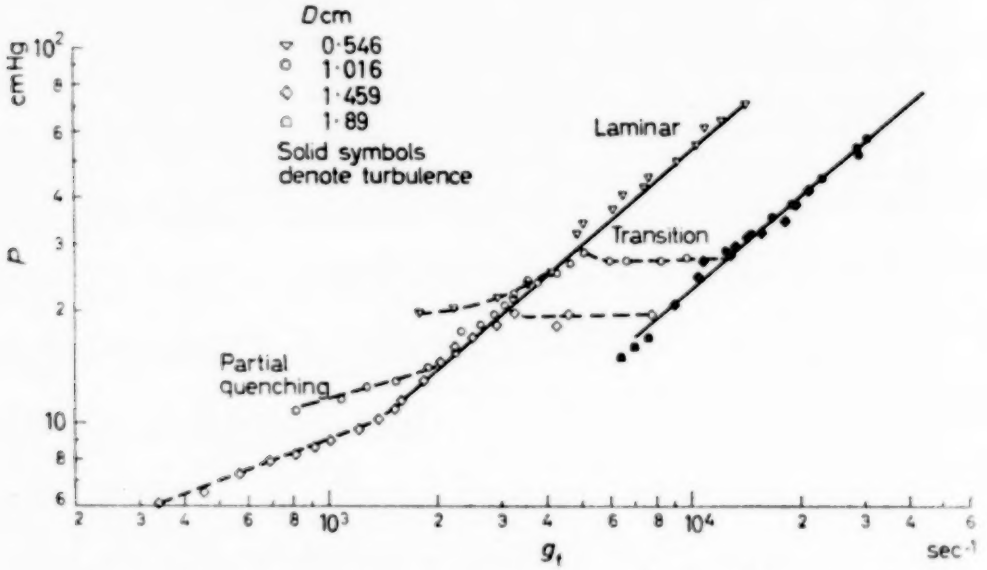


*Figure 2. Flashback of propane–nitrogen–oxygen burner flames. $\phi = 1{\cdot}00$*

log $g_f$ plotted against log $P$ gives two nearly parallel straight lines. The line giving the lower value of $g_f$ for any given pressure is referred to as the line of normal laminar flashback. The line giving the higher value is, accordingly, the line of fully developed turbulent flashback. A large portion

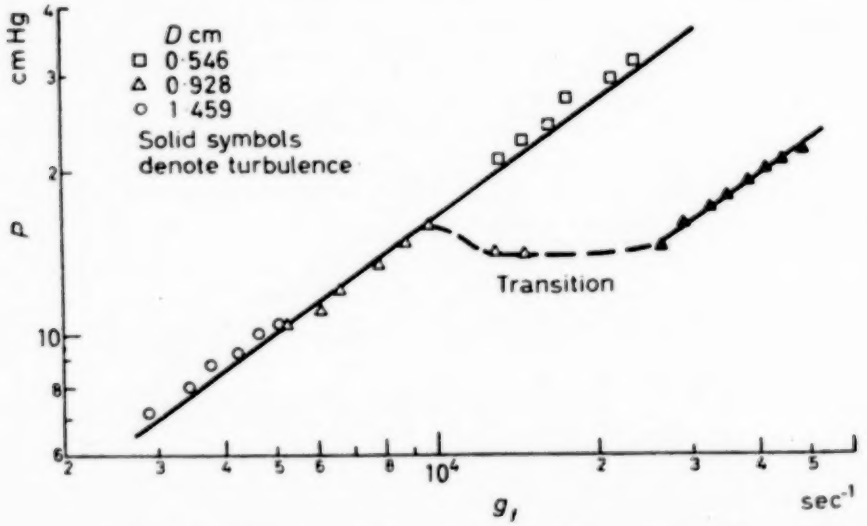


*Figure 3. Flashback of propane–oxygen flames. $\phi = 0{\cdot}85$*

*Equivalence ratio $\phi$ is defined as fuel–oxygen ratio/fuel–oxygen ratio for a stoichiometric mixture.

of the data for any burner will fall along these two lines. At Reynolds numbers below about 400, however, data for each burner deviate from the normal laminar line; as plotted in *Figures 2* and *3* the curve becomes flatter. These flat portions correspond to the region in which flashback

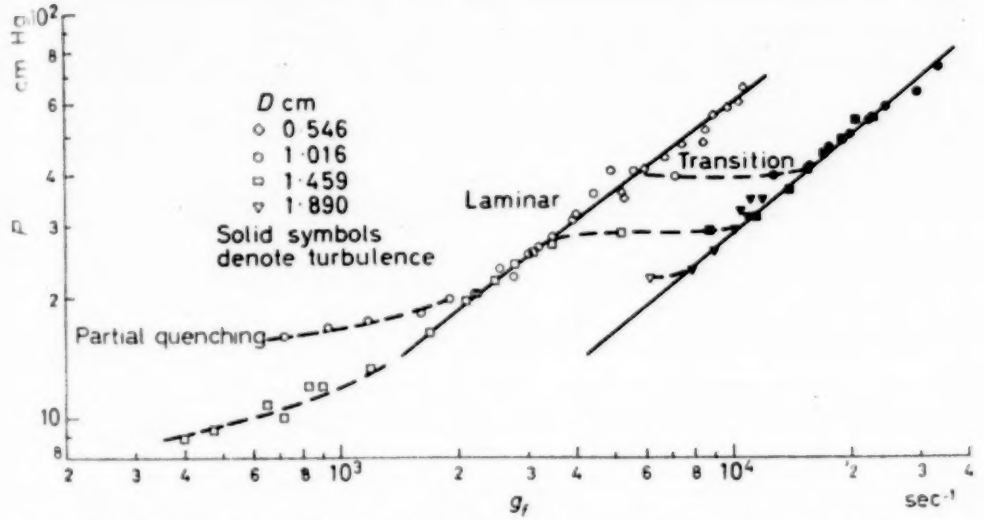


*Figure 4. Flashback of laminar and turbulent hydrogen–air flames. $\phi = 1{\cdot}50$ (38·5 per cent hydrogen)*

ceases to be sharp and tilted flames are observed. The flattening can be thought of as being caused by partial quenching, that is, by a rate of heat abstraction from the flame large enough, relative to the rate of heat production by the flame, to cause flashback at a higher pressure than normal.

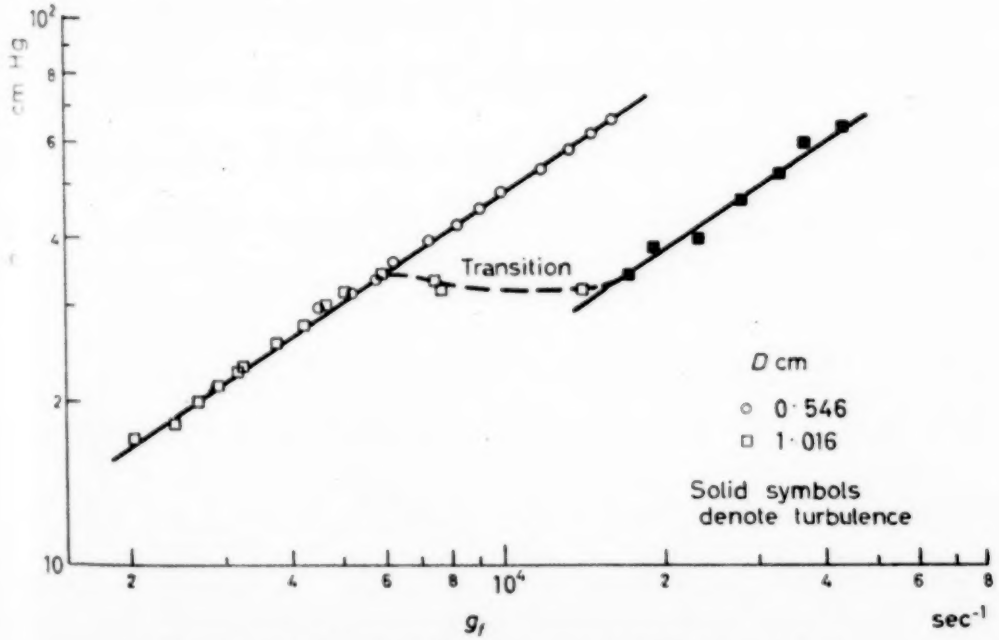


*Figure 5. Flashback of hydrogen–argon 'air' flames. $\phi = 1{\cdot}50$*

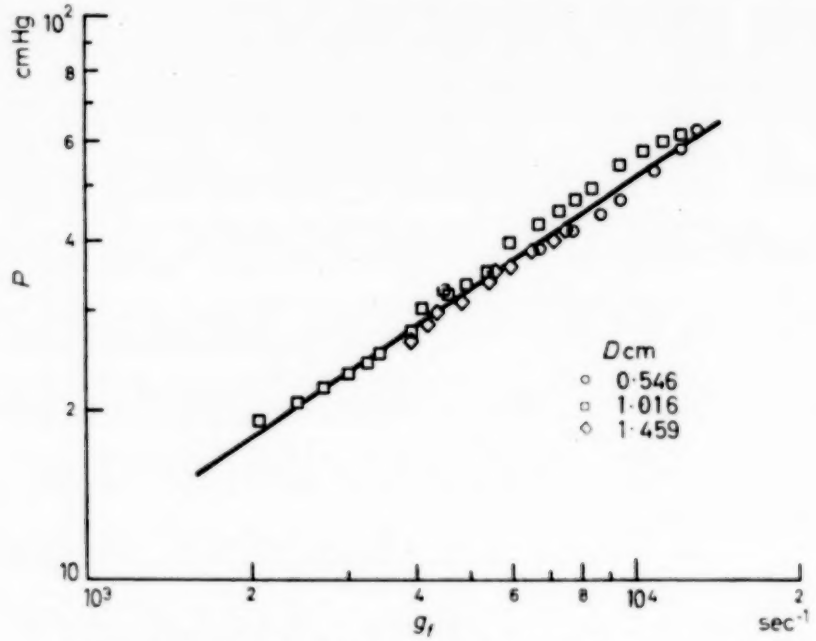


*Figure 6. Flashback of hydrogen–helium 'air' flames. $\phi = 1{\cdot}50$*

At some still lower Reynolds number and pressure, the rate of heat loss would be large enough to cause complete quenching, and the flashback curve would terminate.

Data points for a given burner also depart from the normal laminar line at a higher Reynolds number which represents the beginning of the region of laminar–turbulent transition; this is characterized, it will be

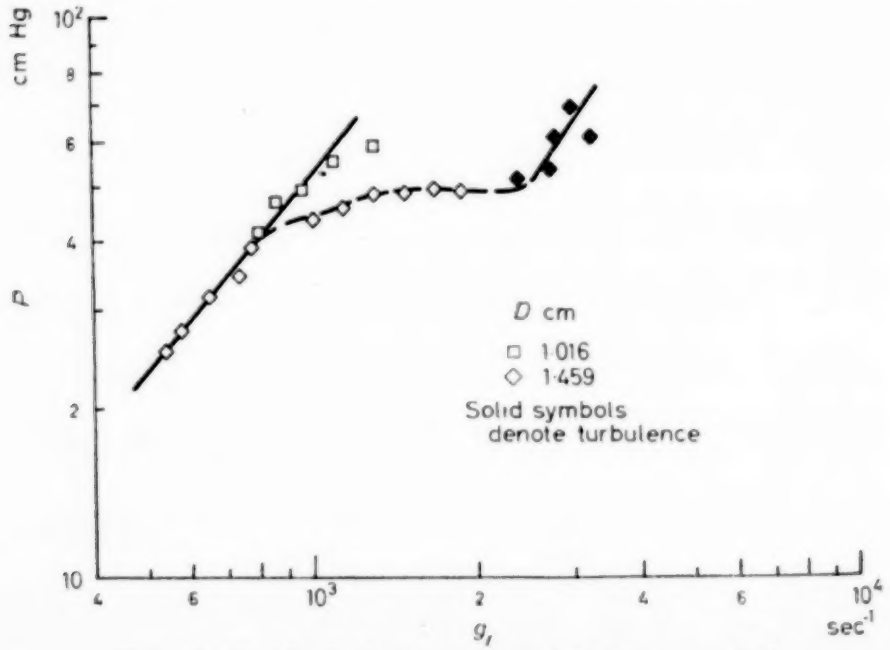


*Figure 7. Flashback of propane–argon 'air' flames. $\phi = 1{\cdot}00$*

recalled, by a nearly constant flashback pressure. Finally, at some still higher Reynolds number flames become steadily turbulent; data points break sharply upward and follow the line of turbulent flashback with further increase in Reynolds number. A few qualitative measurements were made in the absence of a flame with a hot-wire anemometer. It was found that the flow was unsteady over the same range of Reynolds numbers for which flames appeared to fluctuate between the laminar and turbulent condition and for which the pressure at flashback was constant. Thus, the extent of the transition region is not a flame-induced effect.

Flashback curves similar to those shown in *Figures 2* to *7* inclusive have been reported previously at various other equivalence ratios[3, 10, 11]: for hydrogen–air and hydrogen–argon 'air' between about 0·8 and 3·0, for hydrogen–helium 'air' at 1·1 and for propane–oxygen–nitrogen between 0·60 and 1·45. Except for the richest flames studied ($\phi > 2$ for hydrogen flames and $\phi > 1{\cdot}25$ for propane flames), critical flashback gradients were independent of burner diameter. Except for hydrogen flames at an equivalence ratio considerably less than one, the slopes of the normal laminar and turbulent lines were independent of equivalence ratio for any single system.

Flashback data at various equivalence ratios may be cross-plotted to give $g_f$ as a function of $\phi$ at constant pressure. It is found that flashback gradients for hydrogen flames all reach a maximum at about $\phi = 1{\cdot}5$ (38·5 per cent hydrogen) independent of diluent, the maximum occurring at the same $\phi$ for both laminar and turbulent flames. For propane–oxygen–nitrogen flames, the laminar gradient is maximum at about $\phi = 1{\cdot}05$. For turbulent flashback, however, the gradient does not go through a maximum within the measured range of $\phi$. If such a maximum existed it would occur at $\phi > 1{\cdot}25$. This behaviour may be related to the fact that other properties of turbulent burner flames of hydrocarbons, such as turbulent burning velocity, appear to reach a maximum when considerably richer than stoichiometric[12]. The data plotted in *Figures 2* to *7* are for values of $\phi$ near those giving the maximum values for $g_f$ at constant pressure.

*Effect of pressure on critical flashback gradients*

For all systems studied, critical boundary velocity gradients in the normal laminar and fully turbulent regions were found to correlate with pressure raised to some exponent. For hydrogen–air flames, the value of the exponent, $\mathrm{d}\log g_f/\mathrm{d}\log P$, was 1·35 in the laminar region at $\phi = 1{\cdot}50$. The value averaged over several equivalence ratios between 0·95 and 2·25 was also 1·35. The pressure exponent of $g_f(t)$, the critical gradient for turbulent flashback, was 1·31, averaged between $\phi = 0{\cdot}80$ and 3·00. Thus, within experimental error, the relation

$$\frac{\mathrm{d}\log g_f}{\mathrm{d}\log P} = \frac{\mathrm{d}\log g_f(t)}{\mathrm{d}\log P} \qquad \ldots . [4]$$

holds for hydrogen–air flames, except for laminar flames lean of stoichiometric. For both laminar hydrogen–argon 'air' and hydrogen–helium 'air' flames, the average pressure exponent between $\phi = 0{\cdot}90$ and 2·25 was 1·51.

For turbulent hydrogen–argon 'air', a pressure exponent of 1·52 was found at $\phi = 1{\cdot}50$, which agrees well with equation 4. Because of the low density of helium, it was not possible to produce turbulent hydrogen–helium 'air' flames under existing conditions. For propane–oxygen–nitrogen flames, average pressure exponents in the laminar and turbulent regions were respectively 1·13 and 1·11, in agreement, once more, with equation 4. For propane–oxygen flames pressure exponents were about 1·40 in both laminar and turbulent regions. For laminar propane–argon 'air' a pressure exponent of 0·91 was found. Only a few points were obtained in the turbulent region, just sufficient to indicate that the turbulent exponent would be about the same as the laminar. Pressure exponents on $g_f$ for laminar flashback are shown in the first column of *Table 1*.

## DISCUSSION OF RESULTS

### *Laminar flashback*

For many fuel–oxidant systems the relation

$$g_f = cU_b/D_q \qquad \ldots.[5]$$

has been observed, where $U_b$ is the laminar burning velocity and $D_q$ the quenching distance for a given quenching geometry. The coefficient $c$, which also depends on quenching geometry, is independent of pressure but may increase[1, 3] somewhat for a large increase in $g_f$. Logarithmic differentiation with respect to pressure gives

$$\frac{\mathrm{d}\log g_f}{\mathrm{d}\log P} = \frac{\mathrm{d}\log U_b}{\mathrm{d}\log P} - \frac{\mathrm{d}\log D_q}{\mathrm{d}\log P} \qquad \ldots.[6]$$

In order, then, that flame properties over a range of pressure be related by equation 5, it is sufficient that corresponding pressure exponents be related by equation 6.

If one wishes to compare experimental data with equation 6, two points must be considered: first, the value of an experimental pressure exponent for burning velocity can vary widely according to the method of measurement; secondly, pressure exponents for burning velocity and quenching distance should be related by an additional expression

$$\frac{\mathrm{d}\log U_b}{\mathrm{d}\log P} + \frac{\mathrm{d}\log D_q}{\mathrm{d}\log P} + 1 = 0 \qquad \ldots.[7]$$

which has about the same degree of empirical and theoretical validity as equation 6. The use of both equations simultaneously permits $\mathrm{d}\log g_f/\mathrm{d}\log P$ to be calculated in terms of either burning velocity or quenching alone; this serves as a check on the consistency among various pressure exponents chosen.

For hydrogen–air flames, a pressure exponent for $D_q$ of $-1{\cdot}11$ has been observed[11] at $\phi = 1$. If this value and the value of $\mathrm{d}\log U_b/\mathrm{d}\log P$ based on the total area of the schlieren cone[3], 0·23, are used in equation 6 the predicted value of $\mathrm{d}\log g_f/\mathrm{d}\log P$ is in excellent agreement with the average measured value, 1·35. If the pressure exponent of burning velocity based

on pressure rise in a constant volume bomb[15], 0·09, is used in equation 6 instead of the schlieren cone value, agreement with experiment is not as good. One may eliminate $d \log D_q / d \log P$ from equations 6 and 7 and calculate a value of $d \log U_b / d \log P$ from flashback. In this case the value obtained, 0·17, lies between the two measured values.

For propane–oxygen–nitrogen flames, the situation is somewhat different. The measured value of $d \log D_q / d \log P$ is given[16] as $-0{\cdot}93$. The use of this value and a burning velocity exponent based on the total area of the schlieren cone, 0·22, in equation 6 gives a good prediction of the measured flashback exponent, 1·13. If the pressure exponent given by bomb measurements (about 0·10) is used in equation 6 instead of the schlieren cone value, agreement with experiment is not as good. Neither the schlieren burning velocity exponent nor that given by bomb measurements satisfies equation 7 within the experimental error of the measurements. In fact, the value of $d \log U_b / d \log P$ predicted from quenching alone, by equation 7, is actually negative. However, the elimination of $d \log D_q / d \log P$ from equations 6 and 7 gives a predicted value for the pressure exponent of burning velocity very close to that reported from measurements with a constant volume bomb. A possible conclusion would be that the pressure exponent for $D_q$ is too positive by about 0·1.

From the calculations presented above, it appears that equation 6 is approximately correct over a range of pressures, although inconsistencies and uncertainties among pressure exponents make an unequivocal confirmation of this impossible at this time. If it is assumed that equation 5 is approximately followed, one may use burning velocity and quenching distance data to evaluate the coefficient $c$ in the normal laminar region. Since only a rough value is desired, one may use any self-consistent set of values, even though some of the pressure exponents may be questionable. The results over a range of pressure and equivalence ratio are, for hydrogen–air,

$$g_f = 2{\cdot}6\, U_b / D_q \qquad \ldots . [8]$$

and, for propane–oxygen–nitrogen,

$$g_f = 3{\cdot}1\, U_b / D_q \qquad \ldots . [9]$$

where all burning velocities are based on the schlieren total area[3, 11].

According to Lewis and von Elbe (ref. 5, p 286) the flashback of a laminar flame is described by the relation

$$g_f = U_b / \delta \qquad \ldots . [10]$$

which defines the so-called penetration distance $\delta$ as the smallest distance from a cold wall at which $U_b$ attains its normal value. The penetration distance should roughly approximate the dead space caused by the quenching effect of a single wall and should be, therefore, about half the quenching distance between parallel plates. According to equations 8, 9 and 10 that quenching distance is 2·5 to 3 times as great as $\delta$ at flashback, in reasonable agreement with the simple velocity gradient concept. It should be noted that this conclusion depends on the use of quenching distances

equivalent to those measured by a stopped-flow experiment[14, 16]. Quenching distances based on the intersection of flashback and blowoff curves as functions of pressure for various burner sizes would give $c$ values 1·5 to 2 times as great as those given[11] in equations 8 and 9.

*Relation of laminar flashback to flame reactivity and reaction order*— According to A. E. POTTER Jr and A. L. BERLAD[13] a thermal concept of flame propagation leads to the following expressions for the pressure exponents of burning velocity and quenching distance:

$$\frac{\mathrm{d}\log U_b}{\mathrm{d}\log P} = \frac{m}{2} - 1 + \frac{1}{2}r' \frac{\mathrm{d}\log T_u}{\mathrm{d}\log P} + \frac{E}{2RT_u}\frac{\mathrm{d}\log T_u}{\mathrm{d}\log P} \qquad \ldots\ldots[11]$$

$$\frac{\mathrm{d}\log D_q}{\mathrm{d}\log P} = -\frac{m}{2} + \frac{1}{2}r \frac{\mathrm{d}\log T_q}{\mathrm{d}\log P} - \frac{E}{2RT_q}\frac{\mathrm{d}\log T_q}{\mathrm{d}\log P} \qquad \ldots\ldots[12]$$

where $m$ is the overall reaction order, $r'$ and $r$ are the temperature dependences of transport properties in the active and nearly quenched flames (each taken to be about 3/2), $T_u$ and $T_q$ are the temperatures of the active and nearly quenched flames, and $E$ and $R$ are respectively the activation energy and gas constant. One may assume that

$$\frac{\mathrm{d}\log T_u}{\mathrm{d}\log P} = \frac{\mathrm{d}\log T_q}{\mathrm{d}\log P}$$

If it is further assumed that equation 6 may be combined with equations 11 and 12, there results

$$\frac{\mathrm{d}\log g_f}{\mathrm{d}\log P} = m - 1 + \frac{E}{2R}\frac{\mathrm{d}\log T}{\mathrm{d}\log P}\left(\frac{1}{T_u} + \frac{1}{T_q}\right) \qquad \ldots\ldots[13]$$

an expression which is independent of transport properties.

Equation 13 may be solved for $m$ provided that only approximate values of $E$, $T_u$ and $T_q$ are available, since the last term has the nature of a small correction. $T_u$ was taken as the adiabatic flame temperature at 1 atmosphere pressure for a stoichiometric initial mixture at room temperature; $\mathrm{d}\log T_u/\mathrm{d}\log P$ was also evaluated on the basis of adiabatic flame temperatures. $T_q$ was obtained by the empirical relation[13]

$$T_q = 0{\cdot}8\,T_u + 0{\cdot}2\,T_0$$

where $T_0$ is the temperature of the initial mixture. Finally, an activation energy of 40 kcal/mole was assumed for hydrocarbon flames and one of 24 kcal/mole for hydrogen flames[14]. Results are summarized in *Table 1*. In addition, values for propane–air flames are shown (the flashback exponent is actually that for butane–air reported by K. WOHL and C. PETERSON[17]).

Where data are available, a comparison has been made between the reaction order based on flashback, burning velocity and quenching.

For three systems: propane–air, propane–argon 'air' and hydrogen–air, agreement between flashback and quenching is good. For the fourth system, propane–oxygen–nitrogen, the reaction order based on flashback is considerably higher than that based on quenching. This reflects further

*Table 1. Comparison of overall reaction orders from flashback, quenching, and burning velocity*

| *System* | $\frac{d \log g_l}{d \log P}$ | $T_u$ | $\frac{d \log T_u}{d \log P}$ | *m (Flash-back)* | *m (Quen-ching)* | *m (Burning velocity measured in constant volume bomb)* |
|---|---|---|---|---|---|---|
| $H_2$–*air* | 1·35 | 2380 (ref. 13) | 0·017 | 2·25 | 2·17 | 2·10 |
| $H_2$–*argon 'air'* | 1·51 | 2640 (ref. 11) | 0·029 | 2·38 | — | — |
| $H_2$–*helium 'air'* | 1·51 | 2640 (ref. 13) | 0·029 | 2·38 | — | — |
| $C_3H_8$–$O_2$–$N_2$ | 1·13 | 2844 (ref. 13) | 0·025 | 1·94 | 1·63 | 1·98 |
| $C_3H_8$–$O_2$ | 1·40 | 3093 | 0·040 | 2·11 | — | 2·10 |
| $C_3H_8$–*argon 'air'* | 0·91 | 2557 (ref. 13) | 0·026 | 1·68 | 1·71 (ref. 18) | 1·76 |
| $C_3H_8$–*air* | 0·75 ($C_4H_{10}$) | 2253 (ref. 13) | 0·014 | 1·61 | 1·60 (ref. 14) | 1·64 |

the possibility that the value of $d \log D_a / d \log P$ reported by Berlad is too positive by about 0·1. The reaction order obtained from burning velocity alone is 2·22 if the value $d \log U_b / d \log P = 0·22$ obtained from total area schlieren measurements is used. On the other hand, the reaction order based on the value of $d \log U_b / d \log P$ obtained from constant volume bomb measurements is 1·98, in good agreement with that based on flashback. This suggests, once more, that the schlieren pressure exponent is too high. For hydrogen–air flames, on the other hand, the burning velocity reaction order, based on $d \log U_b / d \log P = 0·23$, is 2·38, in fair agreement with results based on quenching and flashback[3], as would be expected from previous considerations. However, the value predicted from bomb measurements, 2·10, is also in fair agreement. In all five cases where a comparison has been made, the reaction order based on burning velocities measured in a constant volume bomb agrees with reaction orders based on flashback or quenching. In two cases (propane–oxygen–nitrogen and propane–air) reaction orders based on burning velocities obtained by burner methods are in strong disagreement with other reaction orders (for propane–air a pressure exponent of about $-0·25$ has usually been obtained with burner

flames). Accordingly, reaction orders based on bomb measurements are shown in the last column of the table. The fact that reaction orders based on flashback are, in most cases, in good agreement with those based on burning velocity and quenching serves to show that equation 6 has some general validity.

According to *Figures 5* and *6* and *Table 1*, flashback data for hydrogen–helium 'air' and hydrogen–argon 'air' are almost identical. Each system gives at any pressure, a value of $g_f$ about twice as great as that observed for hydrogen–air. Burning velocities for flames diluted with helium are known to be considerably larger than for flames correspondingly diluted with argon. Adiabatic flame temperatures, however, are the same. This is a further indication that $g_f$ is independent of transport properties and depends, for similar flames, only on flame temperature.

*Relation between laminar and turbulent flashback*—From *Figures 2* to *5*, it can be seen that at constant pressure, the critical boundary velocity gradient for turbulent flashback, $g_f(t)$, is about 2·8 times that for laminar flashback (this ratio is somewhat composition-dependent for propane–oxygen–nitrogen flames). This increase with turbulence has been observed by others, working at pressures of 1 atmosphere and higher[19-21].

One possible explanation of this effect is that a turbulent burner flame near flashback is stabilized in the so-called laminar sublayer. The existence of this sublayer has generally been inferred on the basis of measurements such as those of radial velocity distribution near the wall[22]. The nature of the flow pattern near the wall is such that any dimensions assigned to the sublayer can only be approximate. Furthermore, it has not been shown that disturbances transmitted from the turbulent core are completely absent from any layer close to the wall. However, one may assume the existence of a nearly laminar sublayer, assign to it rough dimensions and examine flame behaviour in terms of these dimensions.

The thickness of the sublayer $l$ is given[22] by

$$l = 33D\,R_e^{-0.9} \qquad \ldots.[14]$$

This represents a minimum thickness. The actual effective thickness may be as much as twice as great. Since the velocity profile in the sublayer is very nearly linear with radial distance, the critical boundary velocity gradient at flashback for a flame which penetrates the laminar sublayer is $U_e/l$, where $U_e$ is the stream velocity at a distance $l$ from the wall. By this definition, then, expressions for $g_f(t)$ (equation 2) and $l$ may be combined to give an expression for $U_e$ at flashback

$$U_{e,f} = 0{\cdot}75\,\overline{U}_f(t)\,R_e^{-0.1} \qquad \ldots.[15]$$

For Reynolds numbers near 5 000 this becomes, approximately,

$$U_{e,f} = 0{\cdot}3\,\overline{U}_f(t) \qquad \ldots.[16]$$

Since flashback is presumed to occur when the stream velocity equals the normal burning velocity at some distance $\delta(t)$ from the wall, it follows that if a turbulent flame be stabilized in the laminar sublayer, $U_{e,f}$ must

exceed $U_b$. It may be verified, on the basis of present flashback data and suitable burning velocities, that this qualitative condition is met over the entire measured range of flashback.

In a more general sense, if a turbulent flame is to be stabilized in the laminar sublayer, $U_{c,t}$ must exceed $U_b$ at all pressures. It may be assumed that both $U_b$ and $U_{c,t}$ vary as pressure raised to some exponent. It is necessary, then, that $U_{c,t}$ and $U_b$ should have the same pressure dependence. With this assumption, differentiation of equation 15 with respect to pressure along a line of flashback [$R_{c_t} \propto \overline{U}_t(t) \times P$] and substitution of $\mathrm{d}\log U_b/\mathrm{d}\log P$ for $\mathrm{d}\log U_{c,t}/\mathrm{d}\log P$ gives

$$0{\cdot}9\left(\frac{\mathrm{d}\log \overline{U}_t(t)}{\mathrm{d}\log P}\right)_D = \frac{\mathrm{d}\log U_b}{\mathrm{d}\log P} + 0{\cdot}1 \qquad \ldots.[17]$$

By differentiating equation 2 it is seen that

$$\frac{\mathrm{d}\log g_t(t)}{\mathrm{d}\log P} = 0{\cdot}8 + 1{\cdot}8\left(\frac{\mathrm{d}\log \overline{U}_t(t)}{\mathrm{d}\log P}\right)_D \qquad \ldots.[18]$$

Combining equations 17 and 18 gives

$$\frac{\mathrm{d}\log g_t(t)}{\mathrm{d}\log P} = 2\frac{\mathrm{d}\log U_b}{\mathrm{d}\log P} + 1 \qquad \ldots.[19]$$

If one considers known relations among pressure exponents for laminar flames, equations 6 and 7 may be added to give

$$\frac{\mathrm{d}\log g_l}{\mathrm{d}\log P} = 2\frac{\mathrm{d}\log U_b}{\mathrm{d}\log P} + 1 \qquad \ldots.[20]$$

By comparing equations 19 and 20, it is seen that the pressure exponents for laminar and turbulent velocity gradients are equal. This is identical with the experimental findings expressed in equation 4. Thus, the assumption that the turbulent flame is stabilized in the laminar sublayer at all pressures is consistent with experiment. However, the possibility that some other assumption might be equally consistent cannot be excluded.

If it is assumed that the turbulent flame is stabilized in the laminar sublayer, the burning velocity which governs flashback must be the laminar burning velocity. Then, according to equation 10, the threefold increase in critical velocity gradient for flashback which accompanies turbulence must reflect a threefold decrease in the penetration distance and a corresponding increase in the temperature gradient near the wall.

These changes can be made plausible by the following considerations. For a laminar flame, the coefficient governing heat transfer from the flame to the cold wall is nearly constant (its dependence on temperature being neglected) and the temperature profile nearly linear. For a flame stabilized in a field of turbulence which decays toward the wall, such as that which is found in the boundary layer for turbulent pipe flow, the coefficient for heat transfer is not constant, but increases on moving outward from the wall toward the turbulent core. This causes a steepening of the temperature gradient very close to the wall followed by a flattening at larger

distances. If the true penetration distance at flashback were rigidly defined in the terms of the normal burning velocity and flame temperature, the flame could not take any advantage of the change in heat transfer to the wall. If, however, the true penetration distance were measured out to a point where the flame temperature was slightly less than normal, through incipient cooling by the wall, the flame could take advantage of the flattening of the temperature profile so as to penetrate much closer to the wall. It is presumed that the quantity of heat withdrawn from the main body of the flame to bring about the closer penetration would have no perceptible effect in the flame as a whole. The result would be, then, that the temperature gradient would be steeper than for a laminar flame and the penetration distance would be less.

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(*Received February 1958*)

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# *Formation of Polycyclic Hydrocarbons in Diffusion Flames*

J. R. ARTHUR†, B. T. COMMINS‡, J. A. S. GILBERT§, A. J. LINDSEY§ and D. H. NAPIER||

*The polycyclic hydrocarbon content of products from reversed diffusion flames of methane and ethylene, and from the pyrolysis of acetylene have been examined; twenty compounds have been identified and determined. A high degree of similarity between the qualitative compositions of the polycyclic hydrocarbon fractions of the products was found. The experimental evidence is discussed with reference to the mechanism of carbon formation in diffusion flames. It is suggested that acetylene may be the precursor of the polycyclic hydrocarbons, but it is shown that pyrolysis alone is not responsible for carbon formation, and that oxygen intervenes either in the pyrolytic or in other reactions.*

MANY theories[1] have been suggested to explain the formation of carbon in diffusion flames of hydrocarbons in air, but the mechanism is still uncertain although some of the earlier suggestions can now be eliminated. This paper contributes some further information, based on observations of reversed flames, relating to the events occurring in a diffusion flame.

Use of the reversed flame technique in connection with the study of carbon formation has been described before[1] and it has been stated that the isolation of intermediates from such a system is more likely than under normal conditions. The reasons lie in the lower flame temperature and the escape of flame products into a non-oxidizing atmosphere.

It is first necessary to state some of the reported results[1] that are relevant to the present discussion:

(*i*) A black tarry material was formed and collected on surfaces surrounding but not in contact with the flame. Oxygen was found as carbonyl and hydroxyl in both high and low boiling fractions of this deposit.

(*ii*) Acetylene was found in the gaseous products from reversed flames.

(*iii*) Up to 70 per cent by weight of the deposit mentioned in *i* was soluble in carbon tetrachloride. The average molecular weight of this material was between 250 and 600.

(*iv*) Evidence was presented to show that the materials mentioned in *i* were intermediates in the process of carbon formation in diffusion flames.

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In the work reported here a comparison is made between the composition of the hydrocarbon content of reversed flame deposits and that of the products of pyrolysis of acetylene. These results are discussed in connection with the mechanism of carbon formation.

## EXPERIMENTAL

A diagram of the reversed flame apparatus, which was fabricated in Pyrex except for the copper target, is shown in *Figure 1*; a full description of it has been published elsewhere[1]. In these experiments the fuels used were

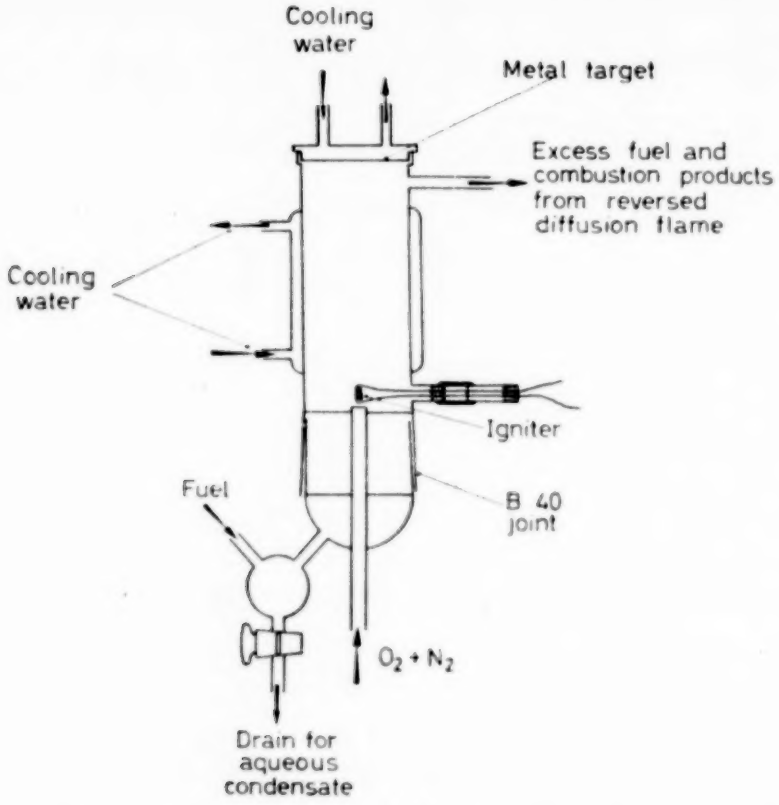


*Figure 1. Reversed flame apparatus*

ethylene and methane, both being dried and freed from carbon dioxide. The composition of these gases is shown in *Table 1*. A stream of dry and carbon dioxide-free air was fed to the port for the reversed ethylene flame, while for the methane flame it was necessary to enrich the air stream with oxygen in order to maintain a stable flame. This mixture contained 30 per cent oxygen (by volume).

*Table 1. Composition of ethylene and methane used in reversed flames (percentage by volume)*

| *Gas* | $C_2H_2$ | $C_2H_4$ | CO | $H_2$ | $C_2H_6$ | $CH_4$ | $N_2$ |
|---|---|---|---|---|---|---|---|
| *Ethylene* | 0·0 | 98·5 | 0·1 | 0·1 | 0·0 | 0·0 | 1·3 |
| *Methane* | 0·0 | 0·1 | 0·0 | 0·0 | 3·3 | 91·3 | 5·3 |

Deposits formed in the apparatus were scraped from the walls, and the aqueous condensate was rejected. This crude material was extracted with acetone and the extract evaporated to small bulk, after which a solution for examination was prepared by adding *cyclo*hexane and again evaporating to small bulk. The solution thus obtained contained the polycyclic hydrocarbons present in the original deposit.

Acetylene to be pyrolysed was prepared from calcium carbide and purified by passing it successively through two tubes packed with glass balls, the first containing copper sulphate solution, the second dilute sulphuric acid, and finally through a soda lime column. The pyrolysis was carried out at 700°C in a clear silica tube; the general arrangement of the apparatus is shown in *Figure 2*. Preliminary experiments at 300° and 500°C yielded

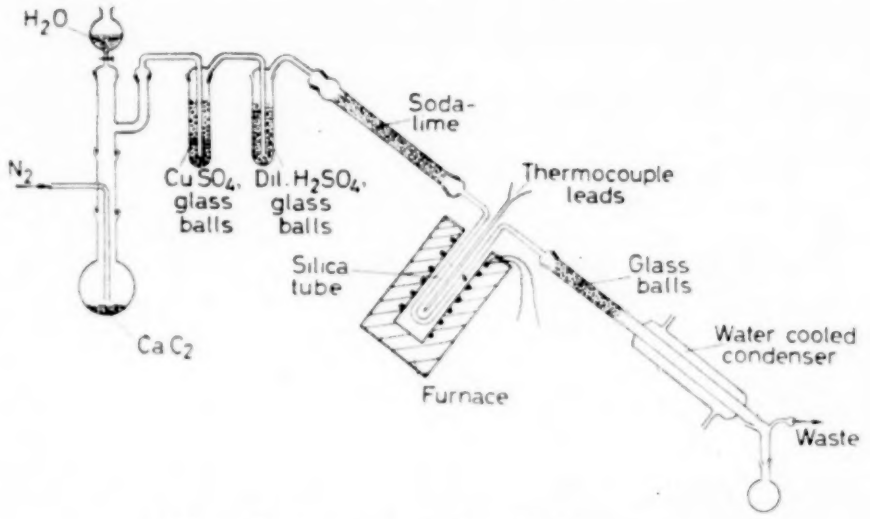


*Figure 2. Arrangement of pyrolysis apparatus*

a small quantity of material, but the reaction at 700°C was vigorous and had to be controlled by addition of nitrogen. The products of pyrolysis were collected on glass balls in a Pyrex tube and by a water-cooled condenser leading into a cooled receiver. The pyrolysis tube and condensers were washed with *cyclo*hexane and the solution was examined.

Aliquot portions of the *cyclo*hexane solutions were examined by a combination of alumina chromatography and absorption spectrophotometry. Details of this procedure have already been published[2, 3].

## RESULTS

The amounts of material extractable with acetone from the products of combustion are shown in *Table 2* as are the quantities of material identified as polycyclic hydrocarbons. Material insoluble in acetone was highly carbonaceous and, as previously reported[1], contained small quantities of hydrogen and oxygen. Oxygen-containing and other compounds present were insoluble in *cyclo*hexane although soluble in acetone, hence a separation was effected. The resulting *cyclo*hexane solution was washed with acid and with alkali before examination.

The products of pyrolysis of acetylene required no preliminary extraction with acetone because they consisted of hydrocarbons (approximately 80 per cent by weight) and carbon only.

*Table 2. Percentages of acetone-soluble material and of polycyclic hydrocarbons in the products*

| *Material* | *Deposit from reversed flame of* | |
|---|---|---|
| | *Ethylene* | *Methane* |
| *Soluble in acetone* | 57·4 | 50·8 |
| *Insoluble in acetone* | 42·6 | 49·2 |
| *Determined polycyclic hydrocarbons* | 8·99 | 18·2 |

The method of examination referred to above was employed and the percentages of polycyclic hydrocarbons found in the *cyclo*hexane-soluble portion of the deposits are shown in *Table 3*. The proportions of polycyclic hydrocarbons was high compared with that found in products of other

*Table 3. Percentage of various polycyclic hydrocarbons in the soluble portion of the deposits*

| *Material* | *Deposit from flames of* | | *Products of pyrolysis of acetylene* | *Molecular weight* |
|---|---|---|---|---|
| | *Ethylene* | *Methane* | | |
| *Naphthalene* | 3·5 | 0·1 | 46·1 | 128 |
| *2-Methylnaphthalene* | | 4·1 | | 142 |
| *Acenaphthene* | 0·2 | 0·3 | | 154 |
| *Fluorene* | 2·8 | 0·2 | 14·7 | 166 |
| *Phenanthrene* | 7·5 | 14·7 | 8·5 | 178 |
| *Anthracene* | 8·4 | 11·6 | 2·0 | 178 |
| *Pyrene* | 1·3 | 35·5 | 5·2 | 202 |
| *Fluoranthene* | 8·4 | 12·4 | 3·5 | 202 |
| *3-Methylpyrene* | 0·3 | 1·2 | *Detected* | 216 |
| *1,2-Benzanthracene* | 1·0 | 1·0 | 3·0 | 228 |
| *Naphthacene* | 0·9 | 0·05 | | 228 |
| *Perylene* | 0·03 | 0·9 | *Detected* | 252 |
| *1,2-Benzpyrene* | | | 0·7 | 252 |
| *3,4-Benzpyrene* | 4·4 | 0·8 | 0·6 | 252 |
| *1,12-Benzperylene* | | 8·3 | 0·5 | 276 |
| *Anthanthrene* | 0·8 | 3·9 | *Detected* | 277 |
| *Coronene* | 0·6 | 2·1 | | 300 |
| *Chrysene* | 0·4 | | 1·5 | 228 |
| *Acenaphthylene* | 59·5 | 2·9 | 13·7 | 152 |
| *Indene* | | | *Detected* | 116 |
| *Total estimated* | 100·03 | 100·05 | 100·0 | |

partial combustion processes (e.g. tobacco smoke, samples of air pollutants, and solutions containing up to 50 000 p.p.m. of single constituents were encountered. This represents an increase of several thousand times the concentration in products from any vegetable matter so far examined.

## DISCUSSION

The outstanding feature of the results given in *Table 3* is that in each case the concentration of one compound was preponderant. From the ethylene flame, 59·5 per cent of the polycyclic hydrocarbons was acenaphthylene,

35·5 per cent from the methane flame was pyrene, and 46·1 per cent from the pyrolysis of acetylene was naphthalene. With the evidence at present available no definite explanation of these facts can be given.

It is also apparent that a similar qualitative pattern is followed in the three sets of results given in *Table 3*. A somewhat similar qualitative pattern is followed by the polycyclic hydrocarbons present in smokes collected from the incomplete combustion of natural gas, butane, butene-1, acetylene and butadiene-1,3. Nine of the polycyclic hydrocarbons determined in the present work were detected by a chromatographic separation[4,5]. Partial combustion of paper and tobacco[6–8] under conditions where smoke was formed also yielded a mixture of polycyclic hydrocarbons with a similar qualitative composition.

The intermediate nature of the material produced from reversed diffusion flames of hydrocarbons has already been established[1]. It has now been shown that apart from oxygen-containing compounds, polycyclic hydrocarbons occur and that these represent either a stage in carbon formation or one route by which carbon is formed. The molecular weights of the polycyclic hydrocarbons from flame products and from pyrolysis of acetylene are shown in *Table 3*, and are in the range (116 to 300) overlapping that of the average molecular weight of the soluble portion of reversed flame deposits (250 to 600).

These observations seem to support the idea of K. RUMMEL and P. O. VEH[9] that carbon formation occurs via polycyclic hydrocarbons (cf. early observations work by Berthelot), and appear to be contrary to G. PORTER'S view[10] that no stable intermediates occur other than acetylene.

Acetylene has been shown to be a universal constituent of gases from reversed flames, and has also been described as an intermediate in carbon formation. In view of the results given in *Table 3*, it could be inferred that the similarity between the composition of the two flame deposits is due to the formation of acetylene and their formation therefrom. This could be explained by assuming that methane pyrolyses as follows

$$CH_4 \longrightarrow C_2H_6 \longrightarrow C_2H_4 \longrightarrow C_2H_2$$

and that higher hydrocarbons degrade until this scheme becomes applicable.

It is of interest to observe that acetylene has also been found among the constituents of the partial combustion of certain vegetable materials (e.g. tobacco)[11].

These observations seem to substantiate the suggestion that acetylene is a key substance in carbon formation in flames. With regard to pyrolysis of other materials (including cellulosic material) and the formation of polycyclic hydrocarbons it seems possible that the small quantities formed are also produced from acetylene.

It has already been established that oxygenated compounds occur in the intermediates[1], and that any mechanism of carbon formation must explain this. It may be suggested that oxygen sensitizes pyrolytic reactions in the process of carbon formation as it has been shown to do in other systems[12]. Oxygen could be responsible for chain initiation and chain termination with the formation of oxygenated compounds.

## CONCLUSION

In the light of the work reported here the criterion of acceptability for a mechanism of carbon formation in flames is that it must reconcile the following three facts:

(*1*) Oxygen-containing materials are intermediates in the process[1]

(*2*) Acetylene is also an intermediate

(*3*) Polycyclic hydrocarbons are formed in diffusion flames.

These observations suggest that the mechanism involves both pyrolyses and reactions in which oxygen intervenes. Further, mechanisms previously propounded can be regarded as inadequate in the following respects:

(*a*) The acetylene mechanism explains neither the presence of polycyclic hydrocarbons nor the formation of oxygen-containing intermediates

(*b*) A theory based on pyrolysis alone does not explain the formation of oxygen-containing intermediates.

It seems most likely that the acetylene which is formed in flames reacts to form material of higher molecular weight. It is further suggested that oxygen may also intervene in the formation of large molecules, e.g. by initiation and termination of reaction chains in pyrolytic reactions, or by partial oxidation of hydrocarbons followed by condensation with elimination of water. Dehydrogenation to carbon, as previously explained[13], will be mainly due to the action of hydrogen atoms.

*The permission of The British Coal Utilisation Research Association to publish this paper is gratefully acknowledged.*

*One of us (J.A.S.G.) wishes to acknowledge the support of the Medical Research Council.*

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*(Received June 1958)*

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# *Use of the Constant-volume Bomb Technique for Measuring Burning Velocity*

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*The method for computing normal burning velocity, called $S_u$, from observed data in constant-volume bomb measurements is developed from first principles. The theory accounts approximately for effects due to the finite velocity of sound, and shows how radius/time measurements may be used to determine $S_u$ for quite fast-burning mixtures. It is shown that the degree of completeness of combustion, important in computing $S_u$, cannot be determined with any accuracy from bomb data, even with simultaneous pressure and radius measurement. Experimental apparatus suitable for constant-volume bomb work at super-atmospheric initial pressures is described, and measurements of flame speed are reported for a stoichiometric methane–oxygen mixture for pressures from 0·1 to 2 atmospheres. Values of $S_u$ computed from the data on flame speed are in fair agreement with values obtained by burner methods.*

## THEORY

### *Introduction*

NORMAL burning velocity, $S_u$, is defined as the velocity at which a flame propagates into an unburnt combustible mixture. One of a number of ways of measuring this property is called the constant-volume bomb technique. In this technique a rigid vessel having a spherical cavity is filled with a combustible gas. The mixture is ignited at the centre, and the position of the flame front and the pressure at the wall determined as a function of time after ignition. From the measurements of flame speed and of rate of pressure rise, the burning velocity may be computed if certain assumptions are made.

This section will develop from first principles the equations needed to compute the burning velocity from the measured values of time rate of change of flame position and/or pressure. The chief difference in the treatment from previous developments[1, 2] lies in taking into account effects due to the finite velocity of sound. The validity of one assumption, attainment of chemical equilibrium, will be shown to remain in question.

After combustion is initiated, the combustion wave proceeds radially outward with the mass of gas inside the flame front increasing due to the combustion that has occurred. Because of the much lower density of the burnt gas, the pressure increase during the first 40 per cent of radial travel is quite small. The unburnt gas backs away from the flame front, due to the large volume change between burnt and unburnt gas. Hence, $S_u$, defined as the velocity of propagation relative to the unburnt gas, is

equal to the difference between the velocity of propagation of the flame front, called flame speed and denoted by $S_s$, and the velocity of the unburnt gas immediately outside the flame front. Inside the flame front the gas velocity is very small. Due to the change in velocity across the flame front there is a small pressure drop across the front. The following assumptions will be made:

(*1*) All molecular species obey the perfect gas law
(*2*) Burnt gases attain chemical equilibrium within a negligible time
(*3*) The process is adiabatic during the period of interest
(*4*) The flame front is spherical
(*5*) The finite thickness of the flame front can be neglected.

In the development possible ways of circumventing the necessity for assumption 2 will be discussed. The following symbols are used in the derivations:

$a$ radius of bomb
$c$ velocity of sound
$E$ expansion ratio; $E=\dfrac{T_b M_u}{T_u M_b}$; $E_i=\dfrac{T_b M_i}{T_i M_b}=E\dfrac{T_u}{T_i}$
$F$ fractional pressure rise function; $F^3=P/P_i-1$
$M$ molecular weight
$n$ weight fraction of original charge which has been burnt at time $t$
$P$ pressure
$r_b$ radius of flame front
$R$ universal gas constant
$S_s$ flame speed in the laboratory coordinate system; $S_s=\mathrm{d}r_b/\mathrm{d}t$
$S_u$ normal burning velocity; velocity of flame front with respect to unburnt gas
$t$ time
$T$ temperature
$V$ volume
$\beta$ a pseudo-Mach number; $\beta=(S_s-S_u)/c_i$
$\gamma_u$ ratio of specific heats of unburnt gas
$\rho$ density

Subscript $b$ refers to conditions in the burnt gas
Subscript $i$ refers to initial conditions
Subscript $u$ refers to conditions in the unburnt gas just outside the flame front.

### *$S_u$ from radius/time data*

Starting from the above assumptions we will derive a formula for computing $S_u$ from measurements of the position of the flame front as a function of time. Let us consider the process for a time $\mathrm{d}t$ during which the flame radius changes from $r_b$ to $(r_b+\mathrm{d}r_b)$. It can easily be shown[3] that

$$S_u\,\mathrm{d}t=-\mathrm{d}V_u/4\pi r_b^2 \qquad \ldots.[1]$$

where $\mathrm{d}V_u$ is the volume of gas which will burn in the time $\mathrm{d}t$. Equation 1 may be rewritten as

$$S_u\,\mathrm{d}t=\frac{1}{4\pi r_b^2\rho_u}\,\mathrm{d}\left(\frac{P_b M_b V_b}{RT_b}\right) \qquad \ldots.[2]$$

The further development of the theory is divided into two parts: Case A, for slow-burning mixtures, where the flame speed is small compared to the velocity of sound in the unburnt gas (say less than $0{\cdot}1\,c$), and Case B, for mixtures such that $S_s > 0{\cdot}1\,c$. In Case A, the pressure in the mixture changes noticeably during the period of interest. In Case B, the pressure inside the flame front remains constant until the sound wave starting at ignition intersects the flame front after travelling to the wall of the bomb and being reflected from the wall. It may readily be computed that this constant pressure period corresponds to an appreciable fraction of the total flame travel. For example, for $S_s/c = 0{\cdot}1$, the point of intersection is at $r_b = 0{\cdot}18a$.

During the time $dt$ the change in the molecular weight and temperature of the burnt gas may be neglected. Recalling that $S_s = dr_b/dt$ it follows that $dV_b = 4\pi r_b^2 S_s\,dt$ and equation 2 then takes the form

$$S_u = \frac{M_b T_i P_b}{M_u T_i P_u}\left(S_s + \frac{r_b}{3P_b}\frac{dP_b}{dt}\right) \qquad \ldots\ldots [3]$$

The momentum equation across the flame front can be written

$$P_b - P_u = -\rho_u W_u (W_b - W_u)$$

where $W_b$ and $W_u$ are the spatial velocities of the burnt and unburnt gas, respectively. Now, $W_b = S_s - S_b$ and $W_u = S_s - S_u$, where $S_b$ is the flame speed relative to the burnt gas. Substitution of these equations into the momentum relation gives

$$P_b - P_u = \rho_u (S_s - S_u)(S_b - S_u)$$

Assuming that the burnt gas comes to rest inside the flame front, $W_b = 0$, and $S_b = S_s$, so that the momentum equation takes the form

$$P_b - P_u = \rho_u (S_s - S_u)^2$$

Using the relations

$$\rho_u = P_u M_u / RT_u \text{ and } c_u = (\gamma_u RT_u/M_u)^{1/2}$$

the momentum equation gives the pressure change across the flame front in the form

$$P_b/P_u = 1 + \gamma_u \{(S_s - S_u)/c_u\}^2$$

which may be rewritten in terms of $\beta$ as

$$P_b/P_u = 1 + \gamma_u \beta^2 T_i/T_u \qquad \ldots\ldots [4]$$

In Case A, where $S_s/c_i < 0{\cdot}1$, $P_b/P_u \simeq 1$. In the following treatment of Case A, we will assume that at any instant the pressure throughout the bomb is uniform so that $P_b = P_u = P$. An estimate of the error caused by this assumption is afforded by equation 4. Using this assumption, equation 3 takes the form

$$S_u = (S_s/E)\,[1 + (r_b/3)\,\{d(\ln P)/dr_b\}]$$

The above equation may be reduced to a simpler form by approximating the second term in brackets. The mass of gas outside the flame front has

been compressed from its original volume $(4\pi/3)\{a^3 - (P/P_i)(r_b^3/E)\}$ to a smaller volume $(4\pi/3)(a^3 - r_b^3)$. Using the assumption of adiabatic compression

$$\ln \frac{P}{P_i} = \gamma_u \left[ \ln \left( 1 - \frac{P}{P_i} \frac{1}{E} \frac{r_b^3}{a^3} \right) - \ln \left( 1 - \frac{r_b^3}{a^3} \right) \right]$$

Since $(r_b/a)^3 \ll 1$, we approximate $\ln(1+x)$ by $x$

$$\ln (P/P_i) \simeq \gamma_u (r_b/a)^3 \{1 - (1/E)(P/P_i)\}$$

Replacing $\{1 - (1/E)(P/P_i)\}$ by $(1 - 1/E)$, we obtain:

$$\frac{r_b}{3} \frac{\mathrm{d} \ln P}{\mathrm{d} r_b} \simeq \gamma_u \left( \frac{r_b}{a} \right)^3 \left( 1 - \frac{1}{E} \right) \simeq \ln P/P_i$$

$$\simeq P/P_i - 1$$

Finally

$$S_u = (P/P_i)(S_s/E) \quad \text{(Case A)} \qquad \ldots . [5]$$

which may also be written

$$S_u = \left[ 1 + \gamma_u \left( \frac{r_b}{a} \right)^3 \left( 1 - \frac{1}{E} \right) \right] \frac{S_s}{E} \qquad \ldots . [5a]$$

During the first stages in burning the term $P/P_i$ is very nearly unity, so that to a very close approximation

$$S_u = S_s/E_i \qquad \ldots . [5b]$$

In Case B, $\mathrm{d}P_b/\mathrm{d}t$ vanishes, and equation 3 reduces to

$$S_u = (P_b/P_u)(S_s/E) \qquad \ldots . [6]$$

However, $P_b$ and $P_u$ are not directly measurable, and their ratio is no longer almost exactly unity. We must determine $P_b/P_u$, $P_u$ and $T_u$ in terms of $P_i$, $T_i$ and $S_s$ in order to complete our knowledge of the meaning of equation 6.

G. I. TAYLOR[1] has obtained a solution for the pressure and velocity distribution of a compressible fluid outside an impenetrable sphere which is expanding at a constant radial velocity in an infinite medium. Conditions outside the flame front correspond to the case treated by Taylor if the velocity of the expanding sphere is taken to be $(S_s - S_u)$, as discussed by R. COURANT and K. O. FRIEDRICHS[2].

The paper by Taylor shows that the pressure just outside the sphere is constant, and somewhat higher than the initial pressure in the medium. He solves the problem in two ways: first by an approximate 'acoustic' theory and then by a numerical solution which includes non-linear effects characteristic of compressible flow theory.

The equation given by Taylor for the acoustic case is (notation altered)

$$(P_u - P_i)/P_i = 2\gamma_u \beta^2/(1+\beta) \qquad \ldots . [7]$$

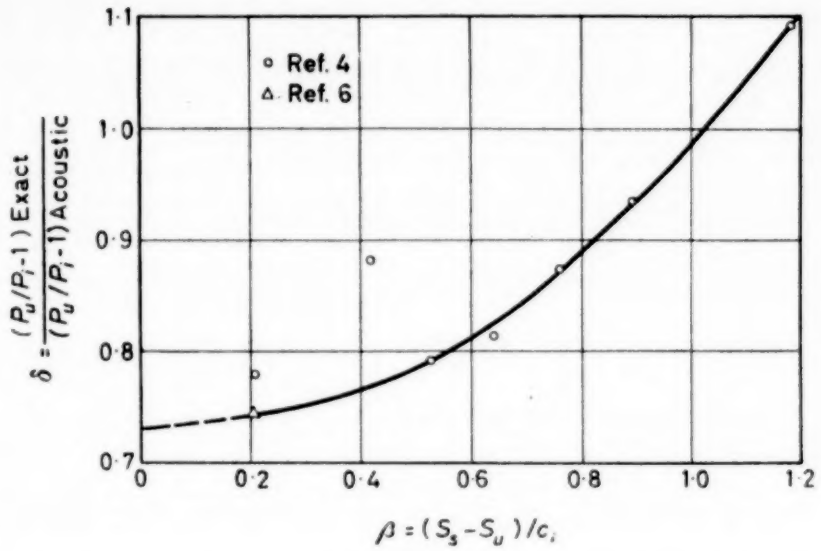


*Figure 1*

In *Figure 1* values of the ratio of the fractional pressure rise, $(P_u/P_i - 1)$, for the 'exact' solution (for $\gamma_u = 1{\cdot}4$) to that found by the 'acoustic' solution (this ratio is denoted by $\delta$) are plotted as a function of the ratio of the velocity of the sphere to that of the speed of sound. The data points indicated by circles in *Figure 1* were computed by Taylor[1]. Because of a numerical discrepancy noted in Taylor's tabulated values for $\beta = 0{\cdot}2$, the authors recomputed the value of $\delta$ for $\beta = 0{\cdot}2$ with the result shown by the triangular data point in *Figure 1*. Examination of this figure makes it

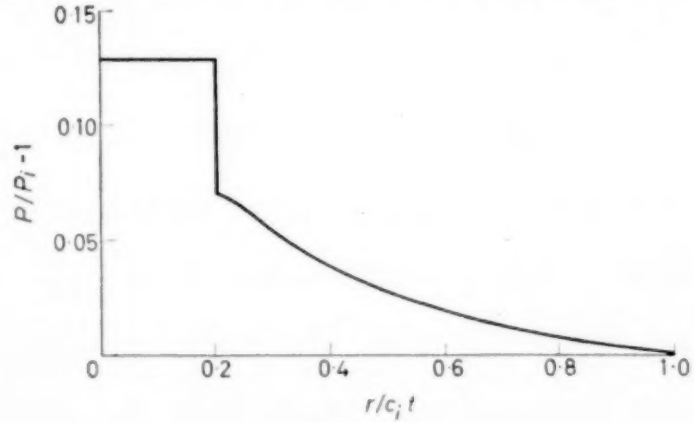


*Figure 2*

seem probable that the values computed by Taylor for $\beta = 0{\cdot}2$ and $0{\cdot}4$ are both in error. Details of the calculations for *Figures 1* and *2* are given by K. C. ESCHENBACH[6]. *Figure 2* shows the pressure distribution in the bomb computed by the 'exact' method, for $(S_s - S_u)/c_u = 0{\cdot}2$. Note that there is a pressure rise of appreciable magnitude across the flame front due to the change in velocity from $(S_s - S_u)$ to zero. The abscissa in *Figure 2* is a dimensionless position parameter. For the case shown, the boundary of the undisturbed gas is always five times farther from the point of origination

of the spherical flame front than is the flame front itself, for all positions of the flame front, i.e. at any time $t$. The bomb is not an infinite medium, so that the pressure wave is reflected at later times and a region of undisturbed gas no longer exists. When the reflected pressure wave intersects the flame front, there is a change in $S_s$.

If one assumes that the ratio of 'exact' to 'acoustic' pressure rises does not change appreciably over the range of values of $\gamma_u$ ordinarily found, $P_u/P_i$ can be computed without repeating the numerical solution from

$$P_u/P_i = 1 + 2\delta\gamma_u\beta^2/(1+\beta) \quad \ldots\ldots [8]$$

The above calculation of $P_u/P_i$ does not apply after the reflected wave intersects the flame front. Until this time, it is expected that $S_s$ will be uniform, unlike the previous case where $S_s$ increases very slightly.

The temperature just outside the flame front, $T_u$, may be found from $T_i$, $P_u/P_i$ and the equation for temperature change in an adiabatic compression. We now have a relation for the burning velocity at the conditions $T_u$ and $P_u$ which may be written as

$$S_u(P_u, T_u) = (1 + \gamma_u\beta^2 T_i/T_u)(T_u/T_i)(S_s/E_i) \quad \ldots\ldots [9]$$

If we assume that burning velocity increases with the square of the initial temperature, as shown to be approximately true by G. L. DUGGER[7], we can convert our equation to a value for $S_u$ at $P_u$ and $T_i$

$$S_u(P_u, T_i) = (S_s/E_i)(T_i/T_u)(1 + \gamma_u\beta^2 T_i/T_u) \quad \text{(Case B)} \quad \ldots\ldots [10]$$

The correction factor for $S_u$ in equation 10 is found by computing $S_u$ approximately from $S_s/E_i$, computing $\beta$, using *Figure 1* to find the multiplier in equation 8, then recomputing $S_u$ using the adiabatic relationship and equation 10.

*$S_u$ from pressure/time data*

In this case we again consider two sorts of processes, where the flame speed is either negligible (Case A′) or significant (Case B′) compared to the velocity of sound. For Case A′ we assume that the pressure is uniform throughout the bomb at any instant of time, so that $P_b = P_u = P$. This involves two physical assumptions: that the pressure of the gas still unburnt is uniform, and that the pressure drop across the combustion wave is negligible.

The gas still unburnt at time $t$ has been adiabatically compressed. Using the equation for adiabatic compression and the definition of $n$ one obtains

$$P_i(1-n)^{\gamma_u} = P[1 - (r_b/a)^3]^{\gamma_u}$$

If $n$ and $(r_b/a)^3$ are much less than one we may approximate this by

$$P_i(1 - n\gamma_u) = P[1 - \gamma_u(r_b/a)^3] \quad \ldots\ldots [11]$$

Substitution of numerical values shows that this approximation is quite accurate for values of $r_b/a$ of interest. From equation 11 and the definitions of $n$ and $E_i$ we obtain

$$n = \{(P - P_i)/P_i\}/\{\gamma_u(E_i - 1)\} \quad \ldots\ldots [12]$$

Repeating equation 1

$$S_u\,\mathrm{d}t = -\,\mathrm{d}V_u/4\pi r_b^2$$

Now

$$\rho_u\,\mathrm{d}V_u = \rho_i\,(4\pi a^3/3)\,(-\mathrm{d}n)$$

Hence

$$S_u = \frac{T_u}{T_i}\frac{P_i}{P_u}\frac{a^3}{3r_b^2}\frac{\mathrm{d}n}{\mathrm{d}t}$$

Using $(T_u/T_i) = (P_u/P_i)^{1-1/\gamma_u}$ and equation 12

$$S_u = \frac{a^3}{3r_b^2}\left(\frac{P}{P_i}\right)^{-1/\gamma_u}\frac{1}{\gamma_u\,(E_i-1)}\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{P-P_i}{P_i}\right)$$

Now let $F^3 = P/P_i - 1$, then

$$S_u = \frac{a^3}{\gamma_u\,(E_i-1)\,r_b^2}F^2\left(\frac{P}{P_i}\right)^{-1/\gamma_u}\frac{\mathrm{d}F}{\mathrm{d}t}$$

From the definition of $n$ we obtain $n = (r_b/a)^3\,(P/P_iE_i)$
Using equation 12

$$F^2 = \left(\frac{r_b}{a}\right)^2\left(\frac{P}{P_i}\right)^{2/3}(1-1/E_i)^{2/3}\gamma_u^{2/3}$$

Then

$$S_u = \frac{a}{E_i\,[\gamma_u\,(1-1/E_i)]^{1/3}}\left(\frac{P}{P_i}\right)^{\left(\frac{2}{3}-\frac{1}{\gamma_u}\right)}\frac{\mathrm{d}F}{\mathrm{d}t}$$

During the first stages in burning the term in $P/P_i$ varies but little from unity, and we obtain finally

$$S_u = \frac{a}{E_i\,[\gamma_u\,(1-1/E_i)]^{1/3}}\frac{\mathrm{d}F}{\mathrm{d}t}\ \text{(Case A')} \qquad \ldots.[13]$$

We will now try to improve the equation for $S_u$ in terms of pressure rise by taking into account the non-uniformity of pressure in the bomb due to finiteness of speed of sound (Case B'). The pressure increase due to burning an increment of gas at time $t$ leads to a rise in pressure at the bomb wall at a later time $t'$, since pressure changes are not propagated instantaneously. Let $t=0$ when $r_b=0$. Obviously no pressure rise will occur at the bomb wall until at least after a time $t=a/c$. When $r_b=a$ the delay time will be 0. We will assume that the delay time varies linearly between these limits and that $P'(t')$ is the actual pressure at the wall which corresponds to $r_b(t)$, where

$$t' = t + [a - r_b(t)]/c \qquad \ldots.[14]$$

Let $F'(t)$ represent the measured value of fractional pressure rise at time $t$. For a small increment in time $\Delta t$, $F'(t)$ changes by $\Delta F'(t)$. Now $F'(t') = F(t)$ and $\Delta F'(t') = \Delta F(t)$. Now $\Delta F'(t') \simeq \Delta F'(t)\,\mathrm{d}t'/\mathrm{d}t$. But from equation 14, assuming that $r_b(t) = S_u t$, we find

$$\mathrm{d}t' = \mathrm{d}t\,(1 - S_u/c)$$

From above and equation 13

$$S_u = \frac{a}{E_i[\gamma_u(1-1/E_i)]^{1/3}} \frac{dF'}{dt}\left(1-\frac{S_u}{c}\right) \quad \text{(Case B')} \qquad \ldots [15]$$

(A somewhat more rigorous derivation of equation 15 is given in reference 6.)

Equation 15 shows that the correction term for $S_u$ based on pressure measurements is noticeable even for moderate flame speeds. The approximations made in its development are seen to make application to fast-burning mixtures ($S_u/c > 0{\cdot}1$) open to considerable question.

*$S_u$ from simultaneous radius and pressure measurements*

We may note from equations 5b and 13 that $S_u$ can be obtained either in terms of flame speed and expansion ratio or in terms of pressure rise and expansion ratio. We can compute this expansion ratio if we believe that combustion products are at thermodynamic equilibrium. On the other hand, we can in principle compute values of $E_i$ from measured values of flame speed and pressure rise by equating equations 5b and 13. This would then enable us to determine burning velocity without the necessity of assumption 2. However, let us see what precision in the measurements of flame speed and pressure rise is necessary to obtain a specified precision in $E_i$. For example, let us take $E_i$ equal to 10, a fairly representative value. A simple calculation shows us that to obtain a precision in $E_i$ of about 10 per cent we must measure $S_u/(dF/dt)$ to within 0·3 per cent, or measure them individually to about 0·2 per cent. However, it appears that attainable accuracy in determining $S_u$ is more of the order of 1 per cent. Hence, even if the fractional pressure rise could be determined to infinite precision (and inherent effects due to the finite velocity of sound would also influence the error), the value of $E_i$ from such a determination could be in error by over 30 per cent. Thus we see that dispensing with assumption 2, while possible in principle, is hardly practicable.

## EXPERIMENTAL METHOD

*Introduction*

In the conventional constant-volume bomb technique the wall of the bomb has a slit window extending along a meridian of the bomb, so that the position of the flame front can be followed by optical means. The presence of the window means that rather low operating pressures must be used. In the present investigation, the position of the flame front was determined by ionization gaps, so that long slit windows were unnecessary. Two bombs were used, one with a spherical cavity of 2·5 in. diameter and the other with a cavity of 10 in. diameter. The vessels were fabricated of Type 410 stainless steel and were designed to withstand a peak working pressure of 5 000 lb/in$^2$ gauge. Two pairs of pointed steel wires were placed in the bomb so that two 0·020 in. gaps were located at different distances from the spark electrodes. About 45 V was applied to each gap; the current flows through the gaps were bucked and measured with an oscilloscope. Arrival of the flame front at a gap was signalled by an appreciable decrease in resistance of that gap. The difference between arrival times at the first

and second ionization gaps was then measured on the oscilloscope trace by comparison with a timing wave. The physical distance between the two gaps was measured before and after an explosion.

This indirect method of determining flame position versus time may introduce certain errors. Possible ways to detect any effect of the ionization gap electrodes on the flame travel itself and ways of checking the sphericity of the flame front are discussed later. It was found that the reproducibility of arrival-time measurements was about 1 per cent, roughly the same as the sensitivity of the measuring equipment.

*Description of procedure*

The procedure in obtaining data will next be briefly described. After a run, the bomb was evacuated to a pressure of less than one millimetre of mercury with a mechanical vacuum pump. The bomb was then dismantled, electrode positions measured, the spark gap checked for centricity and spacing, the bomb reassembled, evacuated again to less than 1 mm pressure, and then filled with the mixture to be studied. For the experiments reported this mixture was methane and oxygen in stoichiometric proportion (two volumes of oxygen to one volume of methane). Such a mixture was prepared in another vessel, mixed and stored for several days before use to ensure thorough mixing. A sample was then taken from this secondary container and analysed for oxygen content to check the proportions in the mixture. The bomb was filled with this gas to the desired initial pressure, connections to the bomb were sealed off and the mixture left undisturbed for a short time. The power supply for the spark source was a bank of eight 0·05 microfarad condensers, charged to 540 V and then switched to series connection and discharged; thus providing a spark energy of approximately 65 mJ. The time measurement was made with a Dumont dual-beam oscilloscope. A sine wave from an audio oscillator was impressed on one of the traces and a signal proportional to the bucked current through the ionization gap circuits on the other. An inductive coil around one of the spark lead wires was used to trigger the sweep at the time the spark fired. Traces from the ionization gaps and the timing wave were recorded photographically.

The position of the ionization gap electrodes was changed and another experiment run to obtain time/distance data at more than two locations. In each case a velocity measurement could be made from a single run by dividing the distance between the gaps by the time required for the flame front to get from one to the other, and assuming that the velocity was constant during this time. This could be checked by determining whether the velocity was the same for other pairs of electrode positions.

*Discussion of errors*

The first question that must be asked when one goes from an optical type to a probe type of measurement on flame experiments is—does the probe change the phenomenon being studied, or, rephrased, does the presence of the electrode wires either accelerate or decelerate the passage of the combustion wave at the location of the ionization gap wires? An experiment

was performed to measure this directly. Five tests were made in which the first two gaps were in a direct line from the centre of the bomb, so that gas which passed through one probe would also pass through the second. Then the wires of the first gap were moved to the opposite side of the bomb, and five more tests were made. The arrival time at the second gap was the same in the two cases within the limit of measurement accuracy.

Another possible source of error in the significance of the results is the question of the initial composition of the gas mixture. This was checked in two ways, first by chemical analysis of the input gas and secondly by measuring the pressure change which occurred in the bomb after the explosion, allowing for condensation of the water formed. A completeness of overall combustion could be calculated by measuring the temperature of the vessel to determine the vapour pressure of the water, and computing the ratio of the pressure change measured to that which would have occurred if combustion had been complete. In all of the runs at one atmosphere and below the completeness of combustion was computed to be $100 \pm 2$ per cent. One possible contaminant was the water vapour formed in each explosion. It is possible that a small amount of water, adsorbed on to the bomb wall, might not have been removed by the vacuum pump during the short pumping time, and later desorbed after the new mixture was placed in the bomb. The possible concentration of water vapour is believed to be less than 1 per cent at 0·1 atmosphere initial pressure, and less than 0·1 per cent at 1 atmosphere.

There was some indication that the early stages of burning were not always exactly reproducible; the time between spark and arrival at the first gap varied somewhat more than that between the two gaps.

With regard to the assumption of completeness of combustion, it was noted that the time for the gap trace deflection to reach an equilibrium value was longer at lower initial pressures.

One indirect test for sphericity of the flame front was made three times. If it is assumed that the asphericity of the flame is circularly symmetrical about the axis of the spark gap, then tests of the flame speed in directions parallel to and perpendicular to the line of current flow in the spark would show up such asphericity. The results of three such comparisons showed that the difference in flame speed between the two directions was less than the experimental error.

The above tests would not reveal effects due to cellular propagation. However, it is believed that cellular propagation would cause greater irregularities in the flame speed than were actually observed.

Since the reaction zone has a finite thickness it is of interest to consider at what point in the flame front the radius is measured. Trace deflection is unmeasurable until the resistance of the gap is less than 100 megohms. Ionization in the flame front is thought to be very small until the temperature reaches about 2 000° K. Hence at the point in the flame front measured by the ionization gap, it is believed that an appreciable fraction of the equilibrium volume change has already occurred. Examination of the traces obtained shows a very sharp change in trace slope at the beginning of deflection. Hence the first noticeable change was taken as the arrival

time. Since the same point is used for measuring both arrival times, valid velocity measurements should be obtained, regardless of the stage at which the measurement is made.

An indirect determination of the effect of finite radius of curvature of the flame front, or of incomplete combustion, may be made by considering whether flame speed changes with stage of the reaction. No change in velocity with radius was observed (until after arrival of the reflected wave), except at a pressure of 0·1 atmosphere, where the flame speed measured between 0·25 and 0·50 in. from the centre was slightly less than that at larger distances. The above constancy of flame speed might tend to indicate that complete combustion occurred in all cases. However, it is conceivable that the combustion proceeds in two stages, with a rapid change to one burnt density and then a very much slower change to a final equilibrium density. The tests made would not be able to detect such an effect and hence the existence of incomplete combustion cannot be ruled out with certainty.

*Results of measurements and calculations*

Some 131 valid explosions were made with mixtures of methane and oxygen at initial pressures ranging from 0·1 to 2 atmospheres. The intial temperature was 25° ± 3°C. The flame speed was computed for each test by means of the time measurement on the oscilloscope and the distance measured between the two gaps. *Table 1* summarizes the measurements and calculations; equation 10 was used to compute $S_u$.

*Table 1. Burning velocity of methane–oxygen mixtures*

| *Pressure* | *(atm)* | 2·0 | 1·0 | 0·5 | 0·2 | 0·1 |
|---|---|---|---|---|---|---|
| $S_u$ | *(m/s)* | 51 | 47·5 | 45·2 | 40·2 | 36·8 |
| $E_i$ | | 12·98 | 12·70 | 12·44 | 12·13 | 11·88 |
| $\beta=(S_u-S_u)/c_i$ | | 0·132 | 0·123 | 0·116 | 0·103 | 0·094 |
| $P_u/P_u$ | | 1·024 | 1·020 | 1·018 | 1·015 | 1·012 |
| $T_u/T_i$ | | 1·008 | 1·007 | 1·006 | 1·005 | 1·004 |
| $P_u/P_i$ | | 1·031 | 1·027 | 1·024 | 1·019 | 1·016 |
| $S_u(P_u,T_i)$ | *(cm/s)* | 399 | 379 | 368 | 334 | 312 |
| $P_u$ | *(atm)* | 2·061 | 1·027 | 0·512 | 0·204 | 0·102 |
| $S_u(approx.)=S_u/E_i$ | | 393 | 374 | 363·5 | 331 | 310 |

$\gamma_u=1{\cdot}365 \qquad c_i=357$ m/s

In *Figure 3* the burning velocity of stoichiometric methane–oxygen is plotted as a function of pressure. It is seen that the five points can be fitted reasonably well by

$$S_u=381\,P^{0{\cdot}085} \qquad \ldots.[16]$$

where $S_u$ is in centimetres per second and $P$ in atmospheres. There have been four quite recent determinations of the burning velocity of methane and oxygen. J. DIEDERICHSEN and H. G. WOLFHARD[8], using a cylindrical burner and the area method of computing $S_u$, measured the burning velocity at pressures from 0·05 to 2 atmospheres and found no significant change in burning velocity with pressure. The average of the determinations of

burning velocity in this reference is 390 cm/s. Two other teams also using burner methods have reported values at one atmosphere for this mixture. G. H. MORGAN and W. R. KANE[9] report 393 cm/s, using a nozzle burner and the area method. J. M. SINGER, J. GRUMER and E. G. COOK[10] report

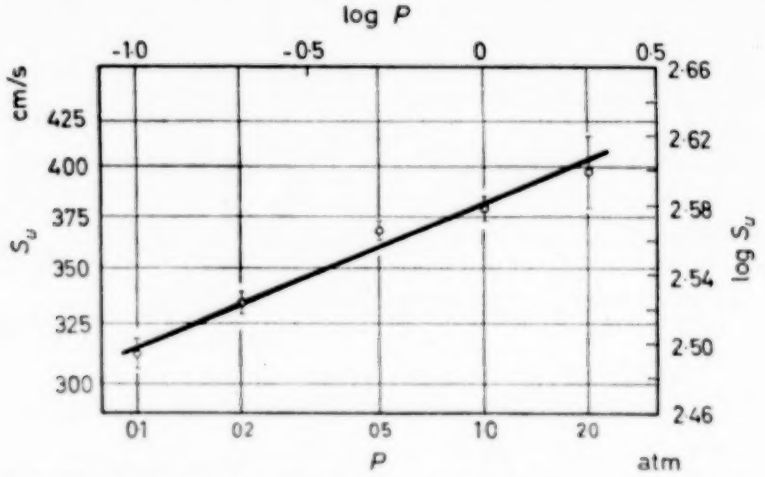


*Figure 3. Burning velocity of stoichiometric methane–oxygen mixture. Solid line given by* $S_u = 381\ P^{0.085}$. *Bars above and below data points represent twice the standard error*

375 cm/s, using a slot burner. All the values at one atmosphere agree quite well with the present determination, 379 cm/s. (The noticeable difference between the value at lower pressures of this investigation and that obtained by Wolfhard will be discussed subsequently.)

The fourth recent investigation is that of J. MANTON and B. B. MILLIKEN[11]. These investigators used a constant-volume bomb, but with the rate of pressure rise method indicated by B. LEWIS and G. VON ELBE[1]. They compute $S_u$ to be 520 cm/s at 0·1 atmosphere and 625 cm/s at 0·25 atmosphere. If these two values are extrapolated to one atmosphere using Manton and Milliken's formula for pressure dependence of burning velocity, one obtains 820 cm/s, in very appreciable contrast to the present result and also those of other investigators. It is believed that the considerations outlined in the theory section explain the difference between the results of reference 11 and the present work.

The difference between the pressure dependence found by Wolfhard[7] and this report could be explained in at least two ways. One explanation would accept Wolfhard's values as correct and ascribe the apparent decrease at lower pressures reported here as due to incomplete combustion. The second explanation would accept the results of this paper as correct and ascribe Wolfhard's relatively high values at low pressures to errors such as those discussed by Singer, Grumer and Cook[10].

## DISCUSSION OF RESULTS

The discussions in the foregoing sections are believed to show clearly the reason for the discordance between constant-volume bomb measurements and burner measurements of burning velocity found for rather fast-burning

mixtures. It is thought that adherence to the considerations suggested in this paper should improve the validity of further measurements made using the bomb method.

However, the difficulty in determining the completeness of combustion is thought to be fundamental to the constant-volume bomb method. For this reason the method is considered to be primarily useful for measuring the burning velocity of mixtures at pressures above the point where a previous measurement has established that a burner method and the constant-volume bomb method produce essentially the same answer. The reasoning behind this step is that, if at one pressure combustion is complete in the time of travel of the flame front through the region of interest, then combustion should also be complete for any higher pressure, since the relative reaction rate is roughly proportional to $P^2/P$. Similarly, burning velocities measured with the bomb method at very low initial pressures should perhaps be regarded with some suspicion until they have been checked by some other means.

In the case of investigators planning to do constant-volume bomb work notice should be taken of the observations of N. MANSON that spherical detonation waves can occur in gas mixtures with strong ignition[12, 13]. Such detonations result in pressures higher than are obtained with deflagrations and good practice would dictate a larger factor of safety than usual due to the effectiveness of shock loads in breaking containers.

*One of the authors (R.C.E.) would like to express his appreciation to the Shell Companies Foundation, Inc., and to the General Motors Corporation for assistance while carrying out this work.*

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*(Received March 1958)*

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# *The Concentration of Hydroxyl and of Oxygen Atoms in Gases from Lean Hydrogen–Air Flames*

W. E. KASKAN

*Measurements of* OH *concentrations in flame gases from lean hydrogen–air flames held on porous burners are reported.* [OH] *is always found to be in excess of equilibrium near the flame and to decay downstream. The decay is formally second order in* OH *and the rate constant is relatively insensitive to pressure, temperature and composition, and has an average value of about* $10^{-13}$ *cm*$^3$*/molecule sec. The effects of the addition of small amounts of nitric oxide have been studied. Data are presented on the relationship between the intensity of light emitted from nitric oxide containing nearly stoichiometric flames and* [OH], *and it is argued that these provide strong evidence that the nitric oxide test for* O *atoms is quantitative. The light-producing reaction is probably*

$$NO + O \rightarrow NO_2 + h\nu$$

*with a rate constant,* $k_{10}$, *equal to* $2 \times 10^{-18}$ *cm*$^3$*/molecule sec. By means of this test it is shown that under all of the conditions studied oxygen atoms and hydroxyl radicals are equilibrated according to the reaction*

$$2OH \rightleftharpoons H_2O + O$$

In a previous paper[1] there were reported measurements of the concentration of hydroxyl, OH, in the flame gases from rich hydrogen–air flames burning on porous metal burners. Hydroxyl concentrations near the flames were always found to be in excess of the equilibrium concentrations and to decay downstream. It was shown in agreement with other work[2] that the kinetics of decay could be satisfactorily explained by assuming a rapid and continuing equilibration of OH and H by the reversible reaction

$$OH + H_2 \rightleftharpoons H_2O + H \qquad \ldots.[1]$$

together with the two three-body recombinations

$$OH + H + M \rightarrow H_2O + M \qquad \ldots.[2]$$

$$H + H + M \rightarrow H_2 + M \qquad \ldots.[3]$$

The present paper concerns the measurement of hydroxyl concentrations in lean hydrogen–air flames. In general the hydroxyl concentrations have been found to be higher than the equilibrium, but not so much so as in rich flames, and to decay downstream. Since it was expected that the decay of hydroxyl would be related to that of other radicals, the nitric oxide test for oxygen atoms was tried in order to obtain additional information on the radical concentrations. As will be shown this test is very probably quantitative in the range of variables employed here, and a rate constant for the light-producing reaction has been obtained.

## EXPERIMENTAL

With a few small differences, the experimental details were as described previously[1]. Since on the lean side there is no diffusion flame between the hot gases and the atmosphere, the burners used were generally simple and not annular as with the rich flames.

Measurements were made at both 1 and 0·45 atmosphere and at temperatures from 1 290 to 1 840°K. As in the previous paper, the temperatures given are the maximum temperatures measured by silica-coated thermocouples, and all measurements were made in a region where the temperature was constant to within about 30°C. The upper temperature limit was arbitrarily imposed because at the higher temperatures the hydroxyl concentrations were so close to equilibrium that it was felt that the decay could not profitably be studied. The lower limit was imposed by the fact that below it the flames became cellular and therefore no longer one-dimensional. Similarly flames with hydrogen–air volume ratios less than about 0·21 are also generally cellular on porous burners, at least at atmospheric pressure. No runs were made with cellular flames.

For the runs with nitric oxide, the addition was made as near to the burner as possible to minimize the time allowed for nitrogen dioxide formation, but it was shown that increasing the time by a factor of about two did not change the results. In addition to the measurement of hydroxyl in these flames, the intensity in a 10 Å wide band at 5 200 Å or at 4 400 Å of the continuum was measured as a function of distance from the burner. In measuring the intensity of emission from low pressure flames, reflection of light from the window at the far side of the flame[1] was blocked and a 10 per cent correction for transmission loss through the near window was applied. Considerable care was taken to ensure that the light was gathered from the same region of the flame gases as was the corresponding hydroxyl measurement. This was done by projecting a beam of light backwards through the monochromator and comparing the path of the beam of light from the slit with that from the hydroxyl source as the two passed over the burner. The system sensitivities in the 10 Å wide bands were determined by a periodic comparison with a radioactively excited phosphor disc which in turn was calibrated with a tungsten lamp.

It was established that when nitric oxide was added there was no measurable absorption at wavelengths near the OH line so that the determination of hydroxyl in the presence of nitric oxide and whatever steady state concentration of nitrogen dioxide existed should have been unaffected. It was also established by the use of a mirror behind a flame in which the continuum was relatively intense that there was no self absorption either at 5 200 Å or at 4 400 Å.

A few runs were made in which heavy water was added to the unburnt gas, and the concentration of OD measured using heavy water in the discharge tube. Liquid heavy water was metered with a small capillary flowmeter and injected into the gas stream just upstream of an evaporator, which consisted of a coil of copper tubing in a hot water (60°C) bath. From the evaporator the gas stream went directly to the burner, which was also heated by a flow of water at about 60°C to prevent condensation of

the heavy water. It was observed on monitoring an OD line that a steady state was reached within ten or fifteen seconds of turning on or off the heavy water, showing that evaporation was complete and that there was no build up of liquid heavy water in the system. The amounts of heavy water were such that the ratio of all the deuterium present to all the hydrogen was about 0·1. The $Q_2$ 10 OD line[3] was used to observe OD. The partition function for OD was calculated[1] as with OH, and the line widths assumed to be the same as for OH. In these experiments the absorption and therefore the accuracy was low due to the relatively small amount of deuterium present and to the larger partition function of OD.

## RESULTS

The conditions of the runs without nitric oxide and the data on the concentrations and decay of hydroxyl are summarized in *Table 1*. The second column gives the volume fuel/air ratio, and the third gives the

*Table 1*

| Run | Hydrogen / Air | $V_{25}$ cm/sec | $T_{gas}$ °K | P atm | l cm | $[OH]_{max.}$ $10^{-16}$ | $[OH]_{min.}$ mol/cm³ | z mm | $\frac{[OH]_{max.}}{[OH]_{equ.}}$ | $k_{OH} \times 10^{13}$ cm³/mol·sec | Correction % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0·210 | 20·0 | 1500 | 1 | 6·2 | 0·318 | 0·044 | 1·5 | 9·4 | 0·85 | |
| 35 | | 36·6 | 1530 | 1 | 9·0 | 0·216 | 0·056 | 2·0 | 4·9 | 1·0 | 0–10 |
| 74a | | 30·2 | 1590 | 1 | 5·0 | 0·189 | 0·070 | 3·0 | 5·0 | 0·95 | |
| 42 | | 20·6 | 1410 | 0·45 | 7·5 | 0·172 | 0·024 | 3·6 | 20 | 1·1 | |
| 44 | | 20·6 | 1410 | 0·45 | 7·5 | 0·080 | 0·031 | 5·2 | 9·8 | 0·9 | 0–10 |
| 68 | 0·224 | 21·2 | 1550 | 1 | 5·0 | 0·244 | 0·030 | 1·5 | 4·6 | 1·25 | |
| 7 | 0·250 | 40·0 | 1560 | 1 | 3·8 | 0·375 | 0·100 | 1·5 | 6·5 | 0·7 | |
| 73a | | 31·9 | 1640 | 1 | 5·0 | 0·470 | 0·083 | 1·5 | 4·6 | 0·8 | |
| 79a | | 31·1 | 1560 | 0·45 | 7·5 | 0·328 | 0·084 | 3·9 | 11·5 | 0·7 | |
| 2 | 0·335 | 6·95 | 1370 | 1 | 6·2 | 0·195 | 0·023 | 1·5 | 19 | 0·55 | |
| 37 | | 5·80 | 1390 | 1 | 14·4 | 0·102 | 0·015 | 2·0 | 8·2 | 0·9 | |
| 3 | | 15·0 | 1500 | 1 | 6·2 | 0·316 | 0·047 | 1·5 | 9·6 | 0·6 | |
| 4 | | 19·2 | 1530 | 1 | 6·2 | 0·352 | 0·069 | 1·5 | 8·2 | 0·55 | |
| 5 | | 23·3 | 1600 | 1 | 6·2 | 0·80 | 0·152 | 1·5 | 11 | 0·5 | |
| 72a | | 25·5 | 1700 | 1 | 5·0 | 0·448 | 0·123 | 1·5 | 3·1 | 0·5 | |
| 34 | | 40·4 | 1750 | 1 | 9·0 | 0·50 | 0·136 | 2·0 | 2·6 | — | |
| 6 | | 62 | 1840 | 1 | 3·8 | 0·95 | 0·305 | 1·5 | 3·0 | — | |
| 48 | | 4·5 | 1290 | 0·45 | 7·5 | 0·095 | 0·020 | 3·6 | 38 | 0·55 | |
| 41 | | 13·6 | 1435 | 0·45 | 7·5 | 0·277 | 0·030 | 3·6 | 19 | 0·6 | ~30 |
| 45 | | 22·8 | 1565 | 0·45 | 7·5 | 0·175 | 0·069 | 6·8 | 5·8 | 0·5 | |
| 47 | | 22·8 | 1565 | 0·45 | 7·5 | 0·248 | 0·065 | 3·6 | 8·3 | 0·45 | |
| 46 | | 32·0 | 1650 | 0·45 | 7·5 | 0·324 | 0·100 | 3·6 | 5·7 | 0·4 | 0–10 |
| 10 | 0·400 | 13·4 | 1530 | 1 | 6·2 | 0·245 | 0·043 | 1·8 | 7·9 | 0·5 | ~50 |
| 8 | | 20·0 | 1580 | 1 | 3·8 | 0·366 | 0·076 | 1·5 | 7·9 | 0·55 | |
| 70a | | 20·2 | 1660 | 1 | 5·0 | 0·383 | 0·111 | 1·5 | 4·8 | 0·3 | |
| 43 | | 12·7 | 1500 | 0·45 | 7·5 | 0·141 | 0·057 | 5·2 | 10·4 | 0·4 | |
| 77a | | 17·2 | 1550 | 0·45 | 7·5 | 0·302 | 0·100 | 3·0 | 15 | 0·22 | 0–10 |

linear velocity of the unburnt gases measured at 25° C and at the pressure of the experiment. The fourth and fifth columns give the gas temperature and pressure, and the sixth the length of the optical path. The seventh and eighth columns give the maximum and minimum hydroxyl concentrations observed in the particular run, and in the ninth column is given the height above the burner at which $[OH]_{max.}$ was determined. The tenth column gives the ratio of maximum [OH] to that at complete equilibrium, as calculated from the data given by B. LEWIS and G. VON ELBE[4]. The last two columns will be discussed later.

As with rich flames[1], the hydroxyl concentrations near the lean flames were invariably found to be higher than the equilibrium values, and to decay downstream. In the lean flames, however, $[OH]_{max.}$ did not exceed the

equilibrium concentration, $[OH]_{equ.}$, by more than a factor of 40, and usually by much less. Furthermore, it can be seen that in some runs (for example Runs 73, 72, 6) the lowest observed concentrations are less than the calculated equilibrium concentration. It is of course highly improbable that [OH] ever dropped below the equilibrium value. Rather this result arises at least partly because of the simplifying assumptions that have been made concerning the line widths[1,5], and probably also because the heat of formation of hydroxyl is somewhat in error. Some recent estimates[6,7] of this heat of formation are lower than the 10 kcal/mole used by Lewis and von Elbe[1]. A lower value leads to higher equilibrium hydroxyl concentrations, but a smaller temperature dependence at constant composition and pressure. Since what is effectively done in the present work is to

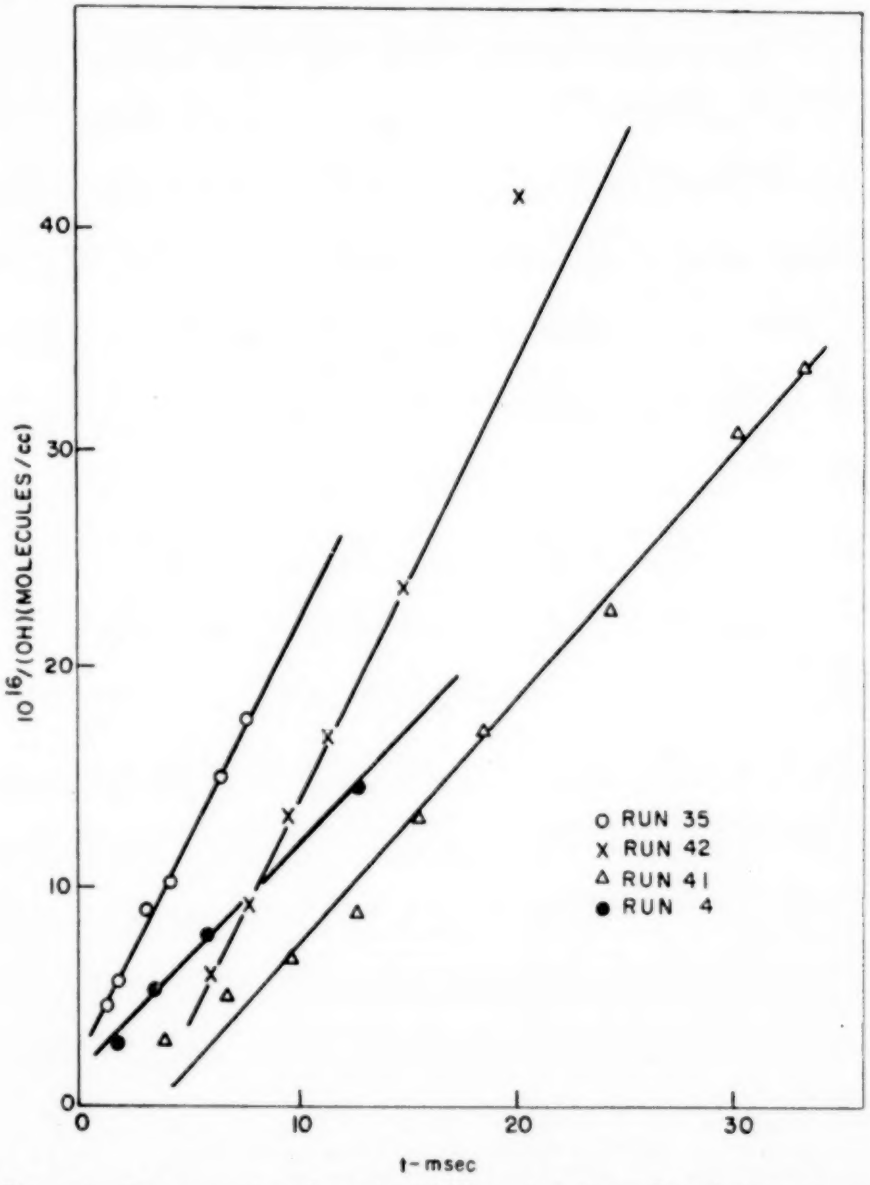


*Figure 1. Representative plots of 1/[OH] against time. Descriptions of runs given in Table 1*

compare the observed [OH] with that under a certain set of conditions[8] at 1473°K, the lower heats of formation would lead to relatively smaller calculated equilibrium concentrations at the higher temperatures.

Except at the highest temperatures, the decay of the hydroxyl concentration was found to be second order in [OH]. This is illustrated for a few of the runs in *Figure 1*. Plots of 1/[OH] against time for the higher temperature runs showed the behaviour to be expected if [OH] were approaching an asymptotic value. Since the measured [OH] were most nearly the equilibrium values for these runs this is not surprising. In the eleventh column in *Table 1* are given the values of the rate constant $k_{OH}$ for the decay assuming the reaction to be

$$OH + OH \rightarrow \text{products} \qquad \ldots [4]$$

where the products are such as to give rise to no more hydroxyl. It can be seen that these all lie within a factor of four of each other, and show no particular dependence of temperature or, at least for the leaner flames, pressure.

In the last column are given a few estimates of the effect of diffusion on the observed rate constant. These corrections were made as described previously[1], assuming only the diffusion of hydroxyl and are to be added to the values in column 11.

The addition of the order of one per cent of nitric oxide to the unburnt gases had no apparent effect on the kinetics of the decay, but increased its rate by an amount at least roughly proportional to the nitric oxide concentration. This statement cannot be made more precise since the amount of

*Table 2*

| *Run* | *Hydrogen Air* | $V_{25}$ | $T_{gas}$ *K* | *P atm* | % NO *in hot gases* | $k_{OH} \times 10^{-9}$ |
|---|---|---|---|---|---|---|
| 74a | 0·21 | 30·2 | 1590 | 1 | 0 | 0·85 |
| 74b | | | | | 0·58 | 1·2 |
| 74c | | | | | 1·04 | 1·3 |
| 74d | | | | | 0·90 | |
| 73a | 0·25 | 31·9 | 1640 | 1 | 0 | 0·8 |
| 73b | | | | | 0·64 | 1·0 |
| 73c, d | | | | | 0·89 | 1·2 |
| 79a | 0·25 | 31·1 | 1560 | 0·45 | 0 | 0·7 |
| 79b | | | | | 0·66 | 0·9 |
| 79c | | | | | 0·56 | |
| 72a | 0·335 | 25·5 | 1700 | 1 | 0 | 0·5 |
| 72b | | | | | 0·69 | 0·6 |
| 72c | | | | | 1·15 | 0·65 |
| 70a | 0·40 | 20·2 | 1660 | 1 | 0 | 0·3 |
| 70b | | | | | 0·56 | 0·4 |
| 70c | | | | | 1·12 | 0·45 |
| 70d | | | | | 1·49 | |
| 77a | 0·40 | 17·2 | 1550 | 0·45 | 0 | 0·22 |
| 77b | | | | | 1·02 | 0·35 |
| 77c | | | | | 1·24 | |

the increase was not too much greater than the experimental error, and was not really sufficient to determine whether nitric oxide also caused a change in the kinetics. The data are given in *Table 2*. The runs are given in groups with the runs in each group differing only in the amount of nitric oxide added. In a few cases the flame temperature was raised 10 or 20°C on the addition of nitric oxide but this small difference has not

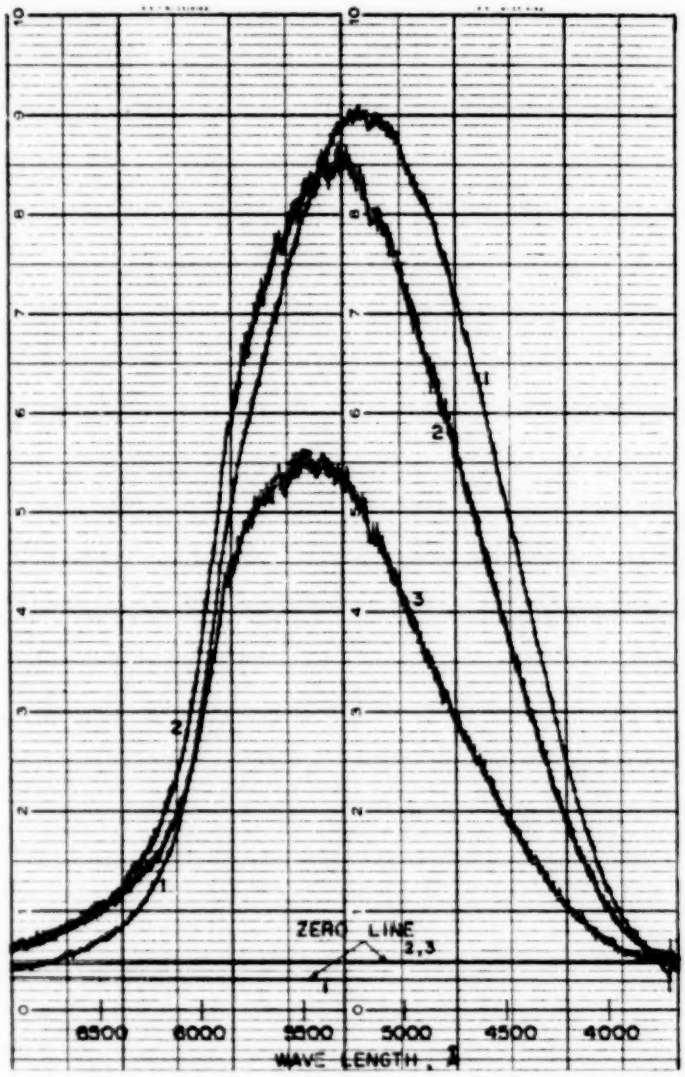


*Figure 2. Emission spectrum of hydrogen–air flame with added nitric oxide, as recorded with a grating monochromator with 1P28 photocell, slit width equivalent to 10 A band pass. Conditions those of run 74 (see Table 1). Curves 1, 2 and 3 recorded at 2, 5 and 10 mm respectively from burner surface. Curves 2 and 3 obtained at the same system sensitivity; curve 1 at 1/4 of this sensitivity. The structure referred to in the text consists of the relatively large fluctuations particularly noticeable in curve 2 from 5 500 to 6 000 Å. The smaller fluctuations throughout all of the curves are statistical noise from the photocell*

been indicated in the table. As before the listed rate constants apply to reaction 4.

The intensity of the light emitted on addition of nitric oxide was a maximum in the reaction zone for all wavelengths from 3 700 Å to 6 500 Å and probably beyond, and decayed downstream. The spectral intensity distribution in this wavelength range of the light emitted from the flame zone was independent of composition and temperature over the ranges covered here. However, as the gases passed downstream the intensity at the longer wavelengths was relatively enhanced for all flames, but more so the leaner the flame. Furthermore, some structure appeared beginning at about 5 000 Å and extending toward the red. This effect is illustrated in *Figure 2* which shows recordings obtained at three distances from the burner for a single flame, that of run 74. The spectral sensitivity of the system was essentially that of the 1P28 photomultiplier tube, so that the intensity in absolute units (energy per unit wavelength range) at the red end of the spectrum is higher than at the lower wavelengths.

In the first experiments in which emission intensity was measured as a function of distance, the measurements were made at 5 200 Å since the signal was at a maximum there. As will be shown later, the light emission at 5 200 was found always proportional to [NO], whether or not the shift of the maximum intensity to the red was noticeable. Since this shift seemed characteristic of flames with excess oxygen, it seemed likely that it was due to the thermal emission of nitrogen dioxide, and that only the emission near the flame was that characteristic of the NO + O reaction. To check this possibility the emission was resolved into two components, the first having that spectral distribution which was always obtained in the flame zone, whether rich or lean, and the second being the difference between the observed emission and the first component. This was done by normalizing the two curves at 4 400 Å. It was found that from 4 500 Å to lower wavelengths the first component and the observed emission always had the same intensity distribution, but that at higher wavelengths the observed intensity fell higher whenever the red shift was apparent. As the gases passed downstream, the intensity of the first component decreased continuously but the second component, the difference, increased slightly in intensity and in some cases reached a steady state, within the error of the measurements. To further check the possibility that this second component was due to nitrogen dioxide, three flames of the same temperature but with different hot gas oxygen contents were examined in more detail. The data are summarized in *Table 3*. In each case the spectrum was recorded at distances progressively further downstream until the second component reached an essentially steady state, which is presumably at least approximately the equilibrium state. Then the relative intensity of the second

*Table 3*

| $P_{NO}$ | $P_{O_2}$ | $P_{NO}P_{O_2}^{\frac{1}{2}}$ | $I$ | $I/P_{NO}P_{O_2}^{\frac{1}{2}}$ |
|---|---|---|---|---|
| 0·0147 | 0·036 | 0·00279 | 1·52 | 545 |
| 0·0085 | 0·072 | 0·00228 | 1·40 | 615 |
| 0·0144 | 0·585 | 0·0110 | 6·2 | 560 |

component was determined as above and compared with the quantity $[NO][O_2]^{1/2}$, which is proportional to $[NO_2]_{equ.}$ at constant temperature. As can be seen in *Table 3*, the intensity of the second component at 5 200 Å is proportional to the quantity $[NO][O_2]^{1/2}$, suggesting that it is actually the thermal emission of nitrogen dioxide.

It should perhaps be emphasized that in this paper nitric oxide is considered to be completely stable against the decomposition to nitrogen and oxygen. Thus the term 'complete equilibrium' as applied to nitric oxide and nitrogen dioxide means that all of the nitric oxide added to the unburnt gases appears as nitric oxide or nitrogen dioxide, but not that an equilibrium is established between 2NO and $O_2 + N_2$.

The possibility that nitrogen dioxide is the emitter of the second component might be further explored by measuring the effect of temperature on the intensity, and by investigating the structure. The first of these is difficult to interpret without a detailed knowledge of the structure of the emitting state, and in particular the excitation energies of the states emitting at the various wavelengths. As to the second, the structure is so weakly defined as to make wavelength measurements very difficult. We have obtained some spectrograms of the emission with a small glass spectrograph. On these the emission appears to consist of a series of equally spaced very diffuse bands starting from about 5 500 Å and extending to the red. There are about 10 bands visible out to ~ 6 500 Å, after which it is difficult to pick out any structure, although the emission is still intense to the limit of the sensitivity of the plate (~ 7 000 Å). There seems to be no obvious relationship between the emission and the absorption spectrum of nitrogen dioxide at room temperature, although again it is difficult to be certain of this because of the diffuseness of the bands. This is not too strong a point in any case since the large temperature difference would be expected to change the fine structure considerably.

Returning to the first component of the emission, the experiments described above show that its intensity should always be obtained by measurement at 4 500 Å and below, and can be obtained at 5 200 Å provided there is little or no oxygen in the flame gases. There is good evidence[9–12] that this emission results from reaction between nitric oxide and O atoms

$$NO + O \rightarrow NO_2 + h\nu \qquad \ldots . [5]$$

The temperatures in the experiments described here were too low to cause measurable decomposition of nitric oxide in the flame gases[13], so that the nitric oxide concentrations should be easily calculable. Thus from reaction 5 the light emission per unit nitric oxide concentration should be proportional to the oxygen atom concentration. On the other hand, if OH and O were always equilibrated in the flame gases by the reaction

$$2OH \rightleftharpoons H_2O + O \qquad \ldots . [6]$$

then [O] could be calculated from the equation

$$[O] = K_c [OH]^2 / [H_2O] \qquad \ldots . [7]$$

where $K_6$ is the equilibrium constant for reaction 6. Thus a plot of $\log I/\{l\,[NO]\}$, where $l$ is the length of the optical path, against the quantity $\log [OH]\,\{K_6/[H_2O]\}^{1/2}$ should be a straight line with a slope of 2.

Some typical plots are shown in *Figures 3* and *4*. In *Figure 3* are data from two runs with a hydrogen–air ratio of 0·400 (compared with the stoichiometric ratio of 0·418), and those in *Figure 4* are for leaner flames. The solid straight lines in the two figures are the same line, which has been drawn with a slope of 2. In *Figure 4*, runs 73b and 73c were identical except for the amount of nitric oxide added, and it is seen that for a given hydroxyl concentration, the emission at 5 200 Å was proportional to [NO]. The conditions of run 73d were also the same except for the nitric oxide concentration, but the light was measured at 4 400 Å and the intensities were multiplied by the appropriate factor to convert them to the intensity which would have obtained at 5 200 Å had there not been interference from nitrogen dioxide emission. Run 74d was a leaner flame with intensities measured at 4 400 Å and corrected as above. The flame of 74d is about as lean as can be burnt in this temperature range without developing cells.

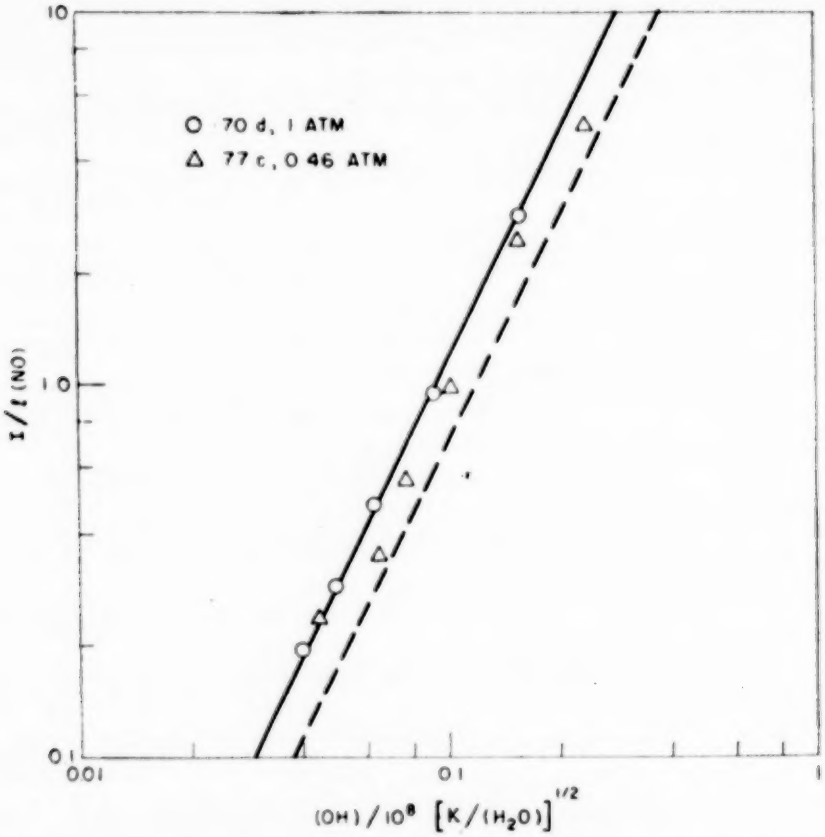


*Figure 3 . Plot of intensity (arbitrary units) at 4 400 Å emitted per unit nitric oxide concentration per unit path length against the square root of oxygen atom concentration as calculated by equation 7 from the measured* [OH] *in two hydrogen/air = 0·400 flames. Conditions of the runs given in Tables 1 and 2. Intensities have been corrected to the intensity at 5 200 Å with no red shift. Dotted line is that on which points for both runs would fall if pressure broadening parameter a' were taken as 0·25 at 1 atmosphere*

The results shown in these figures are typical of all the data obtained in that at atmospheric pressure: (*a*) the data points fell on the line if the intensity was measured at 4 400 Å, (*b*) they fell on the line if the intensity was measured at 5 200 Å and there was very little molecular oxygen in the flame gases, and (*c*) they tended to fall on the line in any case when measurements at 5 200 were made near the flame. On the other hand the data at 0·5 atm fell on a line parallel to the one drawn but displaced to lower intensities. As we shall see this effect is very probably due to some pressure broadening of the OH lines.

Heavy water was added to the flames of runs 34 and 37. Within the rather large experimental error, the [OD]/[OH] ratio near the flame was found to be that of the [D]/[H] ratio and to remain constant as the gases passed downstream.

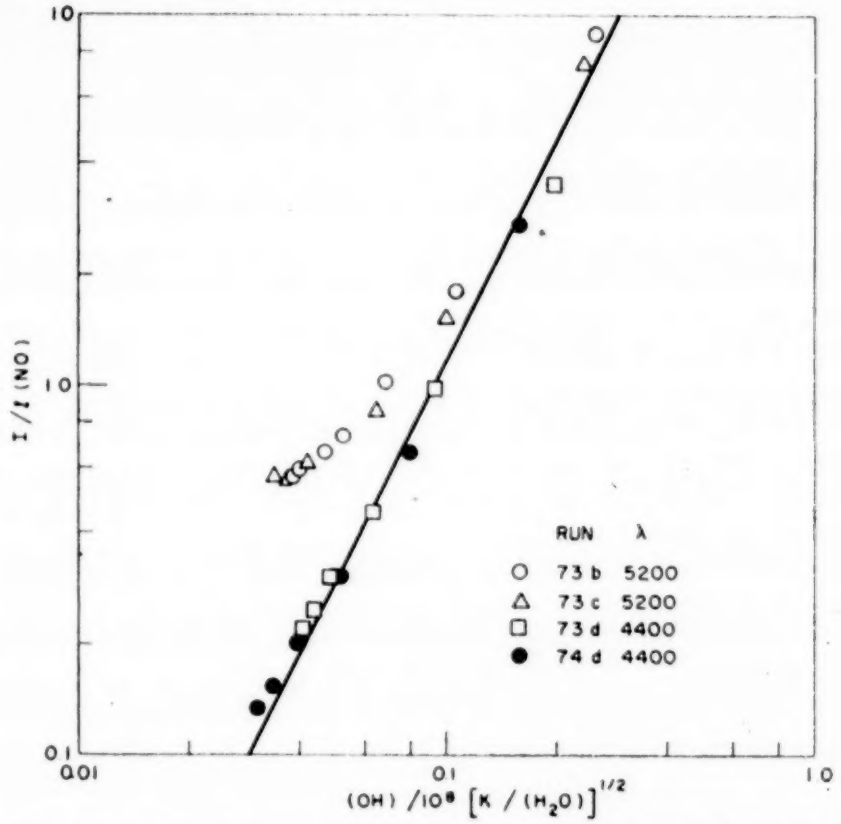


*Figure 4. Plots of intensity (arbitrary units) of light emitted per unit path length per unit concentration of nitric oxide against the square root of oxygen atom concentration as calculated from the measured* [OH]. *Runs described in Tables 1 and 2. Intensities measured at 4 400 corrected to give those at 5 200 in absence of red shift*

## DISCUSSION

There are three points of interest in interpreting the data. The first concerns the relationship between the concentrations of the various radicals, the second concerns the processes by which complete thermodynamic equili-

brium is approached, and the third concerns the validity of the nitric oxide test for atomic oxygen.

(*1*) In connection with the first point it might be noted that in many cases, particularly the faster flames at low pressure, the position of the maximum temperature as determined by a thermocouple in the hot gases lies higher above the burner than the position of the first measurement. In a sense then the measurements also include the tail end of the reaction zone, and any conclusions reached here can be expected to have pertinence further in toward the zone of more rapid reaction.

The 'reaction zone' is difficult to define but from previous work it is known that the temperature in the gas rises rapidly above the surface of the burner and most of the temperature rise has occurred by about 1 mm out from the burner at atmospheric pressure. Because of the difficulty in defining this zone it is equally difficult to try to determine by extrapolation of the data presented here the maximum concentrations of radicals to be expected in the flame itself. It is certain, however, that in all of the cases the hydroxyl concentrations in the region of the most rapid reaction were even higher than the maxima shown in *Table 1*. Thus any flame theory which depends on a calculation of the equilibrium radical concentrations at the flame temperature is most likely to be in serious error.

In rich flames it seems well established[1, 2, 14] that hydrogen and hydroxyl are equilibrated with each other by the reversible reaction

$$OH + H_2 \rightleftharpoons H_2O + H \qquad \ldots\ldots [8]$$

and a measurement of either [H] or [OH] allows the calculation of the other, since $H_2$ and $H_2O$ are both in excess. Furthermore, in rich flames the other two principal reactions in the hydrogen–oxygen scheme

$$H + O_2 \rightleftharpoons OH + O \qquad \ldots\ldots [9]$$

$$O + H_2 \rightleftharpoons OH + H \qquad \ldots\ldots [10]$$

are of considerably less importance since [O] and [$O_2$] are generally expected to be very much smaller than [H] and [OH].

In lean flames of course nothing is known *a priori* of [$H_2$] and therefore of [H], and these are very difficult to measure directly. Thus it was of considerable interest to see what could be learned of the only other radical known to be present, oxygen atoms.

It would appear to be very reasonable, on the basis of the work of others[9–12], to assume that the nitric oxide test for oxygen atoms was quantitative. Actually it is felt that the data reported here for the near stoichiometric flames (hydrogen/air = 0·4, *Figure 3*) afford the best evidence that this test is in fact quantitative under the conditions of the present experiment. This point will be discussed more fully in the last section. If for the present it is assumed to be quantitative, and if it is also assumed that the resolution of the emission into two components is correct, then the data show that O and OH are always equilibrated according to reaction 6 in the presence of nitric oxide. Although schemes can be invented

whereby this equilibration is catalysed by nitric oxide, it seems likely that it is actually effected by reactions involving only molecules in the hydrogen–oxygen system. The equilibration can come about by reaction 6 and its reverse directly, or by the combination of reactions 8 and $-10$, in which case it would be catalysed by H and $H_2$. If the latter were correct, then it would be reasonable to assume at least to a first approximation that H and $H_2$ were also always equilibrated with OH according to the scheme of reactions 8, 9 and 10 and their reverses. If this were so, then the concentrations of H and $H_2$ could be expressed in terms of OH by the expressions

$$[H]_2 = [OH]^2/K_9K_{10}[O_2] \quad \ldots.[11]$$

$$[H] = \{K_8/K_9K_{10}\}\{[OH]^3/[H_2O][O_2]\} \quad \ldots.[12]$$

where the $K$s are the equilibrium constants for the correspondingly numbered reactions. *Table 4* gives some representative concentrations calculated from equations 7, 11 and 12.

Expressions for the rate constants of reactions 8 to 10 have been reported, and although these have generally been determined at temperatures considerably lower than flame temperatures, it is instructive to combine them with the concentrations calculated from equations 7, 11 and 12 to see if the reactions 8 and 10 are fast enough to effect equilibration.

*Table 4*

| *Run* | *Hydrogen Air* | *T* °K | *P* atm | $10^{-16}$ *molecules/cm³ (max.)* [OH] | [O] | [$H_2$] | [H] |
|---|---|---|---|---|---|---|---|
| 35 | 0·21 | 1530 | 1 | 0·216 | 0·024 | 0·021 | 0·0019 |
| 73 | 0·25 | 1640 | 1 | 0·470 | 0·069 | 0·085 | 0·0107 |
| 79 | 0·25 | 1560 | 0·45 | 0·328 | 0·093 | 0·116 | 0·027 |
| 5 | 0·335 | 1600 | 1 | 0·80 | 0·175 | 0·56 | 0·105 |
| 70 | 0·40 | 1660 | 1 | 0·383 | 0·034 | 0·625 | 0·042 |

A value for $k_8$ obtained at low temperatures has been reported by L. AVRAMENKO and R. LORENTSO[15] and this has been approximately verified at flame temperatures by C. P. FENIMORE and G. W. JONES[11]. R. R. BALDWIN[16] has reported the value of a rate constant at 793 °K which could be either $k_8$ or $k_{10}$, but since it is different from the $k_8$ above, it is assumed that his value is appropriate for $k_{10}$. If an activation energy of 6000 cal/mole is taken for reaction 10, $k_{10}$ becomes

$$5{\cdot}4 \times 10^{-14} T \exp(-6000/RT),$$

and the $k_8$ referred to above is

$$7 \times 10^{-12} T \exp(-10000/RT),$$

both in cm³/molecule sec.

Under the conditions of run 74, which is one of the leanest runs and therefore presumably has a minimum of H and $H_2$, it is easily seen that the rates of reaction 10 and its reverse are much lower than those of 8 and $-8$. Thus in the sequence (8, $-10$), which produce one O from two OH, the step $-10$ is limiting and vice versa for the sequence (10, $-8$). Under the assumption that the rate-limiting reactions responsible for the overall decay (to be discussed below) involve either OH or O but not both, then reaction 10 or its reverse must be at least fast enough to keep up with the

decay, and actually considerably faster than this to maintain an approximate equilibration.

With $k_{10}$ given as above, and [H] and [$H_2$] calculated from [OH], at no time during run 74 was reaction 10 or its reverse fast enough to keep up with the decay of radicals, much less effect equilibration. If one were to assume an upper limit for $k_{10}$ which involves a steric factor of 1 but still 6000 cal/mole activation energy, reaction 10 would be fast enough in the early stages of run 74, but marginal in the later stages. This is particularly true with respect to transformation of 2 OH into O, since the absolute rate of decay of OH is larger than that of O. Thus the results obtained suggest that OH and O can actually be equilibrated by reaction 6 as written. Of course, whenever [H] and [$H_2$] are sufficiently large this equilibration will be aided by reactions 8 and 10.

Not much information can be gathered from the heavy water experiments since in each case OH–OD equilibration was already established at the distance of the first measurement. This result is not inconsistent with what has been said above. Thus, for either runs 34 or 37, if the expected rate of OD formation due to reaction −8 is expressed in terms of (*a*) the $k_{-8}$ which can be obtained from the $k_8$ of Avramenko and Lorentso, (*b*) $[H]_{max.}$ from $[OH]_{max.}$ and equation 12, and (*c*) the average $D_2O$ concentration, it turns out that the time required for the gases to reach the plane of the first observation was sufficient to allow somewhat more than the equilibrium OD to form. It might be possible, by increasing the gas velocity (i.e. by nitrogen addition) and by keeping the temperature low, to observe the flame gases before this equilibration sets in.

(2) Turning to the process by which complete equilibrium is approached, the data (*Figure 1* and *Table 1*) show that the decay of hydroxyl was generally found to be second order in OH, independent of temperature in the somewhat restricted temperature range studied, and to have the same rate constant at one-half as at one atmosphere for a particular hydrogen/air ratio, but to increase with decreasing hydrogen/air ratio at either pressure.

Just as with rich flames, in lean flames it is possible to define a function of the concentrations of radicals and hydrogen which has zero time dependence considering only reactions 8 to 10 and their reverses. This function is

$$F_1 = [OH] + 2[O] + 2[H_2] + 3[H] \quad \ldots\ldots [13]$$

As before, the behaviour of this function is unaffected by the addition of reactions 11 to 13 of ref. 1 to the scheme[7]. Thus reactions 8 to 10 cannot bring about the final equilibrium and the function $F_1$ can only change (decrease) due to recombination reactions of some kind.

In general the three recombination reactions considered previously, namely the recombination of H with itself and with OH to form $H_2$ and $H_2O$ respectively and the recombination of O atoms to form $O_2$, are too slow to account for the observed decay. This is easily seen from the fact that the values of $k_{OH}$ in *Table 1* are about the same as that for an efficient

three-body recombination reaction at atmospheric pressure, but the concentrations of H and O assuming equilibration are usually much smaller than those of OH, particularly in the leaner flames, so that three-body recombinations involving them will be correspondingly slower. Thus it appears impossible with the reactions and species so far considered, to account for the disappearance of hydroxyl in the flame gases.

It seems likely that the increase in rate constant with decreasing hydrogen/air ratio can be accounted for by the assumption that there is a single rate-controlling recombination reaction, presumably second order in OH, which is responsible for the decay of the entire pool of radicals as represented by the function $F_1$. The observed rate constant is thus lower in the more nearly stoichiometric flames because in these there exists for any hydroxyl concentration a larger pool of radicals to be drained off by the single reaction. If this is so, then the leaner flames provide more nearly the conditions for the study of this recombination, and the lack of any pressure effect at low hydrogen/air ratio suggests a reaction involving only 2OH (or $H_2O + O$, see below). It is of course entirely possible that the change of $k_{OH}$ with fuel/air ratio is not to be so explained, in which case the pressure independence of the recombination reaction in question cannot necessarily be shown.

Kinetically the reaction of OH with itself is identical with the reaction of O with $H_2O$, because of the relation 7. The only possible reactions which these pairs can undergo and which have not been considered are

$$2OH \text{ (or } O + H_2O) \rightarrow H + HO_2 \quad \ldots\ldots [14]$$

$$\rightarrow H_2O_2 \quad \ldots\ldots [15]$$

The first reaction, apart from being energetically unattractive, does not necessarily accomplish the desired result because the H atom can cause the formation of more hydroxyl. If the second reaction is the significant one, it cannot involve a third body since no pressure effect was observed. Furthermore, it can only involve 2OH, if the $H_2O_2$ formed is in the singlet ground state, because of the spin conservation rules.

On the other hand the reaction involving 2OH is exothermic by 53 kcal/mole so that the stabilization of the hydrogen peroxide must be accounted for. This cannot be done by the emission of light, because presumably the light would be at least partly in the visible range, and the flame gases are not nearly luminous enough for this to be happening. One might postulate that the energy of the reaction is momentarily absorbed by the various degrees of freedom of $H_2O_2$, to be removed by later collision. Alternatively one might postulate an excited state of $H_2O_2$, say a long-lived triplet state, in which case the energy of reaction to be absorbed by the vibrational degrees of freedom of the product molecule would be less, and the reaction of O with $H_2O$ would also be allowed. The excited state could then undergo a quenching to the ground state on a subsequent collision. The subsequent fate of the $H_2O_2$ could be described by the

reactions commonly used in schemes for the pyrolysis and photolysis of hydrogen peroxide,

$$OH + H_2O_2 \rightarrow H_2O + HO_2 \quad \ldots . [16]$$

$$HO_2 + OH \rightarrow H_2O + O_2 \quad \ldots . [17]$$

In this way there can be constructed a mechanism consisting of reactions 15, 16 and 17 which can formally explain the results.

It is conceivable that other mechanisms including $HO_2$, $H_2O_2$, and perhaps $O_3$, could be constructed which would do as well. In view of the speculative nature of the mechanism above, it does not appear very fruitful to pursue the matter further. It must be concluded in any case that no really satisfactory explanation of the disappearance of hydroxyl in the lean flame gases has been found.

The acceleration of the rate of decay by nitric oxide cannot be discussed too quantitatively, since the amount of acceleration was too small as compared with the experimental error to be precisely measured. The most likely reactions responsible would seem to be

$$NO + O + M \rightarrow NO_2 + M \quad \ldots . [18]$$

together with

$$NO_2 + O \rightarrow NO + O_2 \quad \ldots . [19]$$

As previously mentioned, the temperature range in the present experiments was such that no significant decomposition of nitric oxide should have occurred. Thus the sums of [NO] and [$NO_2$] should have been given simply by the amounts of nitric oxide added to the combustible mixtures. If the nitrogen dioxide were present in substantially the amount given by the equilibrium of the reaction

$$2NO + O_2 \rightleftharpoons 2NO_2 \quad \ldots . [20]$$

then in the range of conditions used here [$NO_2$] was always only 1 or 2 per cent of [NO] and the latter can be taken with little error as given by the total nitric oxide added.

The assumption that nitrogen dioxide was present at substantially the equilibrium concentration in most of the runs, even in the presence of oxygen atoms in excess of equilibrium, requires some comment. The only evidence consists of the fact that the second (red) component of the emission was only slowly varying with time. This can be seen for example in *Figure 4* in the data for runs 73b and 73c. The difference between the observed intensities and those given by the straight line is seen to remain approximately constant throughout each run. Since complete equilibrium is certainly being approached it seems quite reasonable to take the nearly steady nitrogen dioxide emission as the equilibrium emission.

This conclusion is surprising, on the other hand, because the rapid conversion of nitric oxide to nitrogen dioxide and vice versa is expected to be catalysed by the radicals present (for example the oxygen atom in reactions 18 and 19) which are in excess of equilibrium. The three-body reaction 20 would be much too slow to be of importance in the time scale of the experiments. Actually it appears probable that nitrogen

dioxide is maintained near the equilibrium concentration by accident. If one considers only reactions 18 and 19, then

$$d[NO_2]/dt = [O]\{k_{18}M[NO] - k_{19}[NO_2]\} \quad \ldots\ldots [21]$$

If $k_{18}$ has a normal value for a three-body collision, for which there is evidence[11], and if $k_{19}$ involves a collision yield of the order of 0·1, for which there is also evidence[17, 18], then the net rate of nitrogen dioxide formation will be zero independent of [O] provided that $[NO_2]$ is approximately the equilibrium value for those flames with considerable excess oxygen. For the more nearly stoichiometric flames where $[O_2]$ is smaller, the concentrations of H and $H_2$ will rise relatively, and additional reactions destroying nitrogen dioxide may become important, thus reducing the steady state nitrogen dioxide. In this way nitrogen dioxide could conceivably be maintained at nearly the equilibrium concentration in spite of the presence of excess concentrations of radicals.

Returning to the acceleration of the decay of hydroxyl by nitric oxide it is of interest to determine whether this can be described by reactions 18 and 19. Since the absolute rate of removal of O atoms is probably about the same for each of these, we can consider only 18 and write

$$\delta k_{OH}[OH]^2 = 4k_{18}M[NO][O] \quad \ldots\ldots [6]$$

or

$$k_{18}M = \delta k_{OH}[H_2O]/4[NO]K_a \quad \ldots\ldots [7]$$

where $\delta k_{OH}$ is the change in $k_{OH}$ on addition of nitric oxide. There was a threefold variation in the values of $k_{18}M$ calculated in this way from the data given in *Table 2*, which could well be within the experimental error. The average value, $10^{-14}$ cm$^3$/molecule sec, is a reasonable value for three-body reactions, but somewhat smaller than that reported by F. KAUFMAN[11] for $M = N_2$. Even so the catalytic effect of nitric oxide in effecting recombinations is probably satisfactorily explained by reactions 18 and 19.

(*3*) In considering the results obtained on light emission on addition of nitric oxide, one should either accept the test as quantitative and treat the results accordingly, or accept the idea of equilibration of reactions 8 to 10 and draw conclusions as to the validity of the test. It is felt the latter course as applied to the results of runs 70d and 77c provides very strong evidence for the validity of the test under the flame conditions in this work.

Referring to *Figure 4*, it is seen that at both one and at one-half atmosphere the data follow straight lines with a slope of 2, but the two lines do not coincide. It will be recalled that in the determination of hydroxyl the simplifying assumption was made that the absorption line was purely Doppler broadened[1, 5]. With this assumption any pressure broadening that does exist will tend to make the measured values at one atmosphere too small as compared with those at half an atmosphere. It can easily be shown[5] that a pressure broadening parameter $a' = 0{\cdot}25$ at atmospheric pressure would make all the data in *Figure 3* fall on a single line indicated by the dotted line in *Figure 3*. This value for $a'$ is within the error estimated for it previously and is consistent with some rough measurements we have made of the line width by measuring both the absorption from a

continuum and of the line source used here, and applying the kind of calculation described in ref. 5. Thus it appears certain that, properly corrected for the pressure broadening, the data at both pressures would fall on the same line.

Since these two runs were only a little to the lean side of the stoichiometric, the concentrations of all four species in excess as calculated from the measured [OH] and equations 7, 11 and 12 are quite appreciable (see *Table 4*). Furthermore the gases approached the plane of the first observation from a region where radical concentrations were even higher. Even allowing for considerable error in the estimates of the rate constants of 8 to 10, these high radical and hydrogen concentrations assure that equilibration will be established, and it seems quite certain that one is justified in calculating [O]

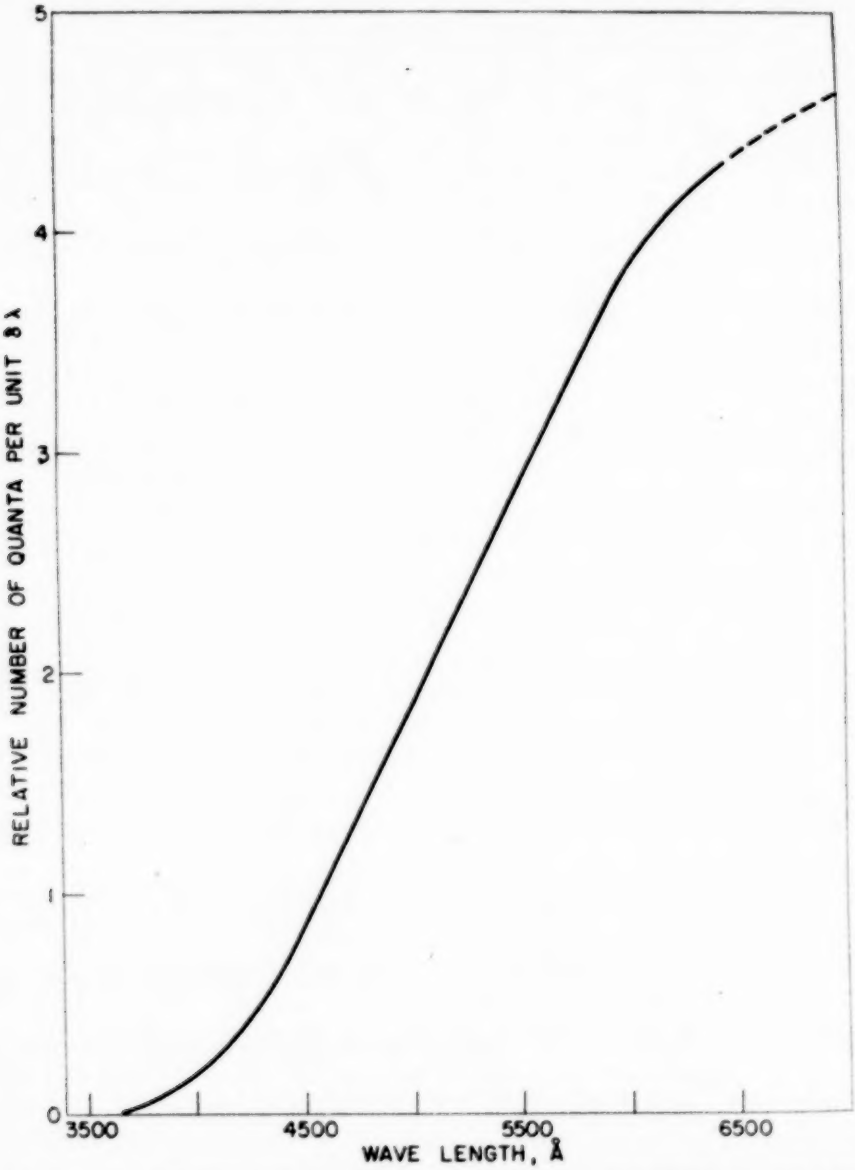


*Figure 5. Relative number of quanta per unit wavelength interval for the first component of emission as a function of wavelength*

from [OH] and equation 7. If this is so, then it follows from the data given in *Figure 3* and the preceding remarks on the effect of pressure broadening that under the conditions of these experiments the nitric oxide test for oxygen atoms is quantitative.

The light-producing reaction can be written

$$NO + O\,(+M) \rightarrow NO_2 + h\nu\,(+M)$$

$$NO + O\,(+M) \rightarrow NO_2^*\,(+M) \rightarrow NO_2 + h\nu\,(+M)$$

The data presented here do not show any effect due to M, any third body, in that neither change of pressure (if line broadening is taken into account) nor of composition seems to affect the test. Thus the reaction involves only oxygen and nitric oxide.

There is still the possibility that $NO_2^*$ is formed and stabilized by the equipartition of the energy of dissociation into the several modes of vibration. Although the spectrum of the continuum seems to be very similar to the fluorescent spectrum of nitrogen dioxide, it is not certain that the excited state in fluorescence is the same as that reached on recombination[19]. The lifetime of fluorescence of the $NO_2^*$ reached by absorption of light is relatively long, about 50 microseconds[20]. Furthermore, the fluorescence is known to be strongly quenched by many other molecules[21], among them $N_2$, $O_2$ and $H_2O$, all of them present at high concentration in our system. Again, since the O atom test works as well at half an atmosphere as at one, the $NO_2^*$ in the flame must be exceedingly short lived if it is the same as the upper state in fluorescence. In any case there is no evidence for quenching which would interfere with the test.

The most likely light-producing reaction is 5, originally suggested by A. G. GAYDON[19], in which radiation is emitted only during the process of a collision. For this type of process the probability of radiation per collision should be simply the probability of spontaneous emission multiplied by the time of a collision, which gives in the present case a value of $10^{-8}$ or $10^{-9}$ per collision if we take 50 microseconds as the lifetime. The rate constant for reaction 5 would then be the collision number times $10^{-8}$ or $10^{-9}$.

Assuming the dashed line in *Figure 3* to represent equilibration of O and OH, it is possible to estimate this rate constant. By comparison with a tungsten strip filament lamp operated at a known colour temperature and situated over the burner in the position of the flame gases, it was determined that the point on the straight line in *Figure 3* at $(I/I)[NO] = 1{\cdot}0$ corresponds to radiation into the total solid angle of $4{\cdot}4 \times 10^9$ quanta per sec per $10^{18}$ [NO]/cm$^3$ of hot gas into the 10 Å band centred on 5 200 Å. Also by comparison with the tungsten lamp, the curve in *Figure 5* was constructed, which gives the relative number of quanta per unit wavelength interval for the continuum. The curve seems to have reached a maximum at about 7000 Å, where the sensitivity of the system became too low to allow any further significant measurements. The ratio of the total number of quanta to those in the 10 Å band is about 350. On the assumption that the complete curve in *Figure 4* would be approximately symmetrical about 7000 Å, the ratio of total quanta emitted to those emitted in the 10 Å band becomes 700. This is a pure guess but it seems unlikely that it is more

than an order of magnitude off. Combining this value with the observed number of quanta emitted, the O concentration from the measured hydroxyl and the known concentration of nitric oxide yields a rate constant of $2 \times 10^{-18}$ cm$^3$/molecule sec for reaction 5 in satisfactory agreement with the value recently reported by F. KAUFMAN[11]. Dividing out a collision number of $6 \times 10^{-10}$ gives a probability of radiation per collision of $3 \times 10^{-9}$, in good agreement with Gaydon's estimate, if the lifetime of fluorescence is used. Thus it can be concluded that the mechanism suggested by Gaydon is very probably correct, and the data are consistent with the collisionally formed $NO_2^*$ being the same excited state as is reached by the absorption of light.

*The author wishes to thank Drs C. P. Fenimore and G. E. Moore for many helpful discussions and Mr W. W. Crotty who performed much of the experimental work.*

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(*Received June 1958*)

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# *Recent Developments and Notes*

## N.G.T.E. SHORT COMBUSTION SYSTEM

THE Second Sir Henry Royce Memorial Lecture was delivered in November 1957 before The Royal Aeronautical Society, by HAYNE CONSTANT, F.R.S., Director of the National Gas Turbine Establishment at Pyestock and this has recently been published [*J. roy. aero. Soc.* 62 (1958) 257]. The lecture was devoted to an account of the major contributions to the development of gas turbines which have been made, not only at the National Gas Turbine Establishment, but also by its predecessor, Power Jets (Research and Development) Ltd, and the earlier Turbine Division of the Engine Department of the Royal Aircraft Establishment. The lecturer considered that it is unrealistic to attempt to differentiate between the contributions of the present Establishment and its parent organization. The period reviewed began in 1937, which year can be regarded as seeing the beginning of effective work on the axial form of jet engine.

In dealing with the progress in solving the problems of combustion in gas turbines, Dr. Constant referred particularly to the developments in the design of the combustion chamber. The most recent and most notable advance has been a chamber having a heat release of $6 \times 10^6$ C.H.U./ft$^3$/atm/h, about three times that of current chambers, without a penalty being paid in other aspects of its performance.

This high degree of compactness has been achieved by incorporating four novel features into this short combustion system. The first of these is the elimination of the compressor diffuser, whereby the length of the chamber is shortened. The secondary air is led straight through the chamber at high velocity to a sandwich mixer, in the cool air passages of which lie the turbine nozzles. Mixing of secondary and primary air takes place in the nozzles, which are at the same time effectively cooled. Uniform peripheral distribution of fuel into the annular primary zone is brought about by dispensing with the normal type of injectors and passing the fuel off the lip of a spinning disc. The turbulence in this primary zone and the strength of the stabilizing vortex are increased by paddle wheels attached to this disc. The lecturer considers that this may prove to be a revolutionary step forward in combustion chamber design.

## INITIATION OF GASEOUS DETONATION

According to a theory which was originally put forward some years ago by K. I. SCHELKIN and later elaborated [*Dokl. Akad. Nauk S.S.S.R.* 23 (1939) 636; *Zh. eksp. teor. Fiz.* 24 (1953) 589], in the transition from gradual combustion to detonation in a gas, the acceleration of the flame front causes the formation of a powerful shock wave which produces detonation at some distance in advance of the flame front.

A further paper by K. I. SCHELKIN on this subject develops his theory to take into account certain phenomena which are present in the vicinity

of the origin of detonation [*Zh. eksp. teor. Fiz.* 29 (1955) 221; *Ref. Zh. Mekh. No. 11 (1958) Rev. 7251*]. It is now assumed that cases may occur in which the temperature rise in the shock wave is insufficient to produce detonation. When this condition is present, according to the author, at the instant when the flame reaches the high temperature region beyond the shock wave, the velocity of the flame front greatly increases. This causes the formation of a second shock wave which may lead to detonation directly in advance of the flame front (Translation by Ministry of Supply).

### STRUCTURE OF OXIDIZED CARBON

J. D. WATT and (the late) ROSALIND E. FRANKLIN have reported some results of work carried out at Birkbeck College, London, to determine which features of the structure of carbon most influence its combustion properties [*Nature, Lond.* 180 (1957) 1190]. The influence, on the structure of carbon, of various forms of controlled partial combustion was studied by x-ray diffraction methods. Samples of carbon containing 2 to 20 per cent by weight of oxygen were prepared either by heating in oxygen at 300° to 450° C for several days or by reacting with ozone at room temperature.

X-Ray powder-photographs of the initial carbon, the oxidized carbon, and the product after degassing at 1 000° C, show that the structural changes resulting from the two methods of oxidation are very similar. The oxidized carbon is characterized in each case by a disappearance of single layers and by a marked increase in the layer stacking. The most vulnerable part of the structure is that which exists as single graphitic layers; the disordered part is less vulnerable but is still more reactive than the parallel groups, the amount of which remains unchanged throughout the treatment. This appears to indicate that the combustion process does not consist, as is sometimes suggested, of a gradual consumption of the layers, starting from the edges and proceeding inwards. There would rather appear to be a tendency for the layers either to remain intact or to be wholly consumed, isolated layers being particularly susceptible to total destruction.

### DETONATION TEMPERATURES

F. C. GIBSON, M. L. BOWSER, C. R. SUMMERS, F. H. SCOTT and C. M. MASON, of the U.S. Bureau of Mines, Division of Explosives Technology, Pittsburgh, have recently described an electro-optical method of determining detonation temperatures in high explosives [*J. appl. Phys.* 29 (1958) 628]. The method consists in sampling the optical radiation from the interior of a detonating solid explosive charge by introducing a transparent plastic rod axially into the charge at the time of fabrication. The plastic rod 'pipes' the radiation from within the charge into the optical system of the spectrograph. Since the rod probe extends axially into the end of the charge, the radiation source is from a zone of high confinement and should be characteristic of the 'infinite' slab and representative of steady-state conditions with the charge near the core.

The radiation was analysed by a grating spectrograph, using four bands 100 A wide and 600 A apart. The radiation intensities were used to calculate the colour temperature within the detonating explosive. The apparatus

was calibrated by a radio-frequency-excited lamp known to have grey body radiation. The explosive charges were vacuum-impregnated with propane to replace the air in the intergranular voids in order to eliminate light emission from the air shock.

The detonation temperature of nitroglycerine was found to be 4 000°K for high-order detonation, of velocity about 7 500 m/s, and 3 200°K for low-order detonation, of velocity 1 500 to 2 000 m/s.

### INJECTION AND COMBUSTION OF LIQUID FUELS

The preparation of a monograph was undertaken in 1950 on the *Injection and Combustion of Liquid Fuels*, by the Battelle Memorial Institute for the Aeronautical Research Laboratory, Wright-Patterson Air Force Base, Ohio. This has now been issued as a mimeographed document of about 740 pages and constitutes a major contribution in the way of review of material in the literature relating directly to the fundamental physical phenomena involved in steady flow processes in high-intensity combustion chambers (*W.A.D.C. tech. Rep. No. 56–344, A.S.T.I.A. Docum. No. AD 118 142*, Wright Air Development Center, U.S. Air Force, March, 1957).

The subjects dealt with are: (*i*) Atomization of liquid fuels: mechanism and methods of atomization, design of atomizers, spray analysis; (*ii*) Ballistics of droplets and dynamics of dispersion; (*iii*) Evaporation of droplets: thermodynamics and kinetics of evaporation, single droplet evaporation, evaporation of a moving droplet, spray evaporation; (*iv*) Fluid dynamics, equations, turbulence, hydrodynamic recirculation; (*v*) Homogeneous combustion: laminar flame propagation, turbulent flames of premixed gases, stability limits of premixed flames, ignition of combustible mixtures; (*vi*) Heterogeneous combustion: droplet combustion, diffusion flames.

An extensive bibliography is appended to each section.

### THE TUYÈRE COMBUSTION ZONE OF THE BLAST FURNACE

Investigations on the tuyère zone of the blast furnace have been made over a considerable period, mainly with regard to gas composition and temperature measurements along the line of the tuyère axis. In the past few years, however, attention has been directed to the physical movement of the coke particles caused by the jet action of the air blast. In the work of J. F. ELLIOTT, R. A. BUCHANAN and J. B. WAGSTAFF [*Trans. Amer. Inst. min. (metall.) Engrs* 194 (1952) 709] a vigorous recirculation of particles in the tuyère zone was revealed by high-speed cine films taken through the tuyère hatch. It was shown that a raceway exists opposite each tuyère of the blast furnace and this is formed by the jet effect of the air emerging from the tuyère. The raceway appears to consist essentially of a turbulence in which coke particles are recirculated at high speed, it is probably three-dimensional and all the raceways of a furnace probably overlap. It would seem that about half the coke in a furnace is consumed in this region, so that movement of the stock column may well be controlled by raceway behaviour. In a later paper J. B. WAGSTAFF described studies of the raceway induced in a bed of particles which have been made on models, but

under non-combustion conditions [*Trans. Amer. Inst. min. (metall.) Engrs* 197 (1953) 895].

The tuyère combustion zone has now been studied under combustion conditions by means of raceway measurements and gas-composition surveys by J. TAYLOR, G. LONIE and R. HAY [*J. Iron St. Inst.* 187 (1957) 330]. An experimental rectangular shaft furnace, 4 ft wide, 2½ ft deep, and 8 ft high was used, with tuyères spaced 15 in. apart to correspond to the 6 in. tuyère at 5 ft centres in the modern blast furnace. The effects of variables such as air velocity and temperature, tuyère diameter, and coke size were investigated.

It is concluded from this investigation that in the large modern blast furnace the tuyère combustion zone is characterized by a raceway and that this effectively demarcates the zone in which consumption of coke and reoxidation of iron, silicon, etc., takes place. In the earlier smaller blast furnaces a raceway was frequently not developed. The effect of coke size is consequently different according to the size of the furance. In a stationary bed the penetration of oxidizing gas decreases with decrease in coke size whereas under raceway conditions penetration increases. This would suggest that the use of smaller sized coke would be advantageous in modern furnaces.

The correlation between raceway and combustion zone is important because raceway can be investigated comparatively easily and the results are directly applicable to the combustion zone.

### PYROLYSIS OF HYDROCARBONS IN SHOCK WAVES

Experiments on the pyrolysis of some simple hydrocarbons in which the heating was produced by shock waves, are described by E. F. GREENE, R. L. TAYLOR and W. L. PATTERSON, Jr, of Brown University, Providence, R.I. [*J. phys. Chem.* 62 (1958) 238]. The heating by this means is homogeneous, the heating time is extremely short, about $10^{-5}$ sec, and the cooling time is fairly short, about $10^{-4}$ sec. With such conditions the products isolated after the shock are likely to be more representative of intermediates in the pyrolysis reaction than with other ways of heating.

The experiments were carried out in a 3 in. i.d. shock tube similar to one described earlier by E. F. GREENE [*J. Amer. chem. Soc.* 76 (1954) 2127]. The hydrocarbons investigated were methane, ethane, ethylene, acetylene and benzene, in a temperature range of 1 600° to 2 500° K, under conditions of temperature and concentration as nearly equivalent as possible. In the main series of experiments the hydrocarbons were mixed with argon to reduce the average heat capacity of the gas in order to achieve the final temperatures of 1 900° and 2 500° K. The pyrolysis products were condensed at the temperature of liquid nitrogen and analysed by infra-red and gas chromatographic methods. The results obtained are regarded as supporting the proposal of G. PORTER that the formation of solid carbon and hydrogen in the pyrolysis of hydrocarbons above about 1 000° C proceeds by a series of degradations to acetylene which then simultaneously polymerizes and loses hydrogen to form carbon [*AGARD Memo. A G 13/M9* (1954); *Fourth Symposium (International) on Combustion*, p 248.

Williams and Wilkins: Baltimore, 1953]. The authors of the present paper suggest that diacetylene, $C_4H_2$, is likely to be the first intermediate formed from acetylene.

### HYDROGEN–OXYGEN REACTION

W. FORST and P. A. GIGUÈRE, of the Department of Chemistry, Laval University, Quebec, have recently reported the discovery that hydrogen peroxide acts as a strong inhibitor of the second explosion limit of the hydrogen–oxygen reaction [*J. phys. Chem.* 62 (1958) 340]. The effect was studied at 447°C, in a reaction vessel with a clean Pyrex surface, by the withdrawal technique, as a function of the composition of the mixture.

The results obtained show a quadratic dependence of $p_1/p_2$ (ratio of the inhibited limit to the normal second limit) on $f_{H_2O_2}$ (concentration of hydrogen peroxide). This is discussed in the light of the generally accepted mechanism for the uninhibited second explosion limit of the hydrogen–oxygen reaction. It is found that the simplest scheme which can account for the results is obtained by adding the two reactions

$$H_2O_2 + H = H_2O + OH$$

and

$$H_2O_2 + OH = H_2O + HO_2$$

to the generally accepted mechanism for the second limit.

### LIQUID MONOPROPELLANT FLAME

A major difficulty in studying the combustion of double-base propellants is that of stabilizing a stationary laminar flame. A possibility of circumventing this and obtaining information on the burning mechanism of such propellants is to investigate liquid nitrate esters as models for the solid propellants. D. P. NEEDHAM and J. POWLING a few years ago established a stationary flat flame of ethyl nitrate at atmospheric pressure but this flame was not sufficiently stable to allow analysis of the initial reaction zone [*Proc. Roy. Soc. A* 232 (1955) 337]. An attempt to investigate this early reaction zone has now been made by R. STEINBERGER and V. P. SCHAAF, of the Hercules Powder Company, Allegany Ballistics Laboratory, Cumberland, Md, who have developed a method for stabilizing a stationary flat flame of ethylene glycol dinitrate [*J. phys. Chem.* 62 (1958) 280]. They have devised a fritted disc burner and obtained a stable flame at a pressure as low as 50 mm of mercury. At this pressure the primary reaction zone was sufficiently lengthened, about 4 mm, to allow detailed exploration with fine-wire thermocouples of 0·0001 in. diameter, the finest that were obtainable. The resulting temperature profile, analysed in terms of volumetric heat release rate, shows the presence of two distinct reaction zones which can be correlated with the visible features of the flame. The visible part of the flame is orange in colour and is separated from the liquid surface by a dark zone which is approximately 2 mm thick at 53 mm pressure. The authors consider that this dark zone must be regarded as a reaction zone, but to what extent vaporization may take place is an open question.

### EFFECT OF SONIC VIBRATIONS ON HEAT TRANSFER FROM FLAMES

S. R. TAILBY and I. BERKOVITCH, of the Department of Chemical Engineering, Battersea Polytechnic, London, have described a research on the effect of sonic vibrations on heat transfer from town gas flames [*Trans. Instn chem. Engrs, Lond.* 36 (1958) 13]. The apparatus described in an earlier investigation by M. A. SALEH and S. R. TAILBY [*Trans. Instn chem. Engrs, Lond.* 31 (1953) 36] formed the basic equipment for the present research and measurements were made of the heat transfer from a town gas diffusion flame to a vertical water-cooled tube built up from separate units equipped for calorimetry and radiometry, the lowest units consisting of six calorimeters, each 4 in. high, followed by three 1 ft units. The heating tube was used at a constant height of 5 ft.

Sonic vibrations at frequencies of 600 and 1 700 c/s were applied to the gas stream. The effect was essentially to increase the heat transfer by factors of 2 to 3 in the lower parts of the tube, notably in the bottom 16 in. section and to produce a slight fall in heat transfer rate in the upper part of the tube. It is regarded that this latter effect in the upper part of the tube is not a primary effect but one due to fall in temperature. The fall in temperature may be consequent upon an increased rate of hydrocarbon cracking, which is endothermic.

The vibrations also lowered the position in the tube of maximum heat transfer and radiation heat transfer, they increased flame emissivity in the lower part of the tube at the higher sound pressures, and they shortened the flame.

### INITIAL OXIDATION OF HYDROCARBONS

The first of a series of papers on the point of oxygen attack in the combustion of hydrocarbons has been published by C. F. CULLIS, F. R. F. HARDY and D. W. TURNER, of the Department of Chemistry, Imperial College of Science and Technology, London [*Proc. Roy. Soc. A* 244 (1958) 573]. The work is an attempt to reconcile the contrasting effects of hydrocarbon structure on the ease of initial attack and on overall oxidizability; the anomalous behaviour seems to be due to the two opposing effects of tertiary C—H groups, at which apparently oxidation starts most readily, but whose presence, nevertheless, reduces the ease of oxidation of the molecule as a whole. This paper describes a $^{14}C$-tracer study designed to determine the origin of carbon monoxide, one of the products of combustion, and the fuel investigated was 2-methylpentane, which contains a tertiary as well as primary and secondary C—H bonds.

Methods were devised for the synthesis of 2-methylpentane labelled in each of the skeletal positions in turn. Combustion of these compounds with an insufficiency of oxygen was carried out at 242° and 380° C. The carbon monoxide formed was oxidized by preferential combustion over copper oxide and the specific activity of the resulting carbon dioxide was then determined. At both temperatures carbon monoxide was found to be derived principally from the 3- and 4-positions. Oxidation at a tertiary centre is unlikely to lead to the production of appreciable amounts of carbon monoxide and this may account for the low yields from the 2-position.

It is concluded that the relative amounts of carbon monoxide from the 3-, 4- and 5-positions provide a reliable indication of the relative probabilities of initial attack at these points.

### OXIDATION OF OLEFINIC HYDROCARBONS

A series of three papers from the Donnan Laboratories, Department of Inorganic and Physical Chemistry, The University of Liverpool, has recently been published describing work which is part of a systematic study being made of both the low temperature gaseous combustion and the solution catalysed oxidation of olefins. The present papers deal with the gas-phase oxidation of propylene, butene-2, and hexene-1, and are respectively by J. D. MULLEN and G. SKIRROW; A. BLUNDELL and G. SKIRROW; and G. SKIRROW [*Proc. Roy. Soc. A* 244 (1958) 312, 331, 345].

The reaction between propylene and oxygen between 340° and 400°C, examined in a static system, was found to be of the degenerately branched-chain type, and acetaldehyde is mainly responsible for the branching. The aldehyde is probably produced by the decomposition of a peroxide which is the initially formed molecular product. There is an unusual relationship between reaction rate and hydrocarbon concentration which clearly indicates partial suppression of the reaction by excess hydrocarbon.

The gas-phase oxidation of butene-2 was examined over the temperature range 289° to 395°C. No difference in behaviour of the *cis* and *trans* forms could be detected. At the higher temperatures the reaction resembled that of the oxidation of propylene in the shape of the pressure/time curve and in the identity of many of the reaction products. A striking feature of the oxidation at lower temperatures is the pressure drop following an induction period and preceding the maximum rate of pressure increase. Peroxides were found to be produced during the period of pressure decrease and their formation appears to be at least a partial explanation of the pressure decrease. It is suggested that a peroxide precedes the formation of acetaldehyde, and that branching occurs largely through reaction of acetyl radicals produced from the acetaldehyde. As with propylene, the inhibiting effects produced by excess olefin are attributed to the formation of less reactive or unreactive allylic-type radicals, and the addition reactions of olefin at higher olefin concentrations lead to polymerization and a low or negative overall pressure change. The characteristics such as inhibition and polymerization shown by both propylene and butene-2 are peculiar to the oxidation of the olefins and not apparent in the oxidation of paraffinic hydrocarbons.

The oxidation of hexene-1 was investigated at 263°C. The main features of the analytical data are in general agreement with the overall reaction schemes suggested for the oxidation of propylene and butene-2. The unusual form of dependency of reaction rate on hydrocarbon pressure obtained when the maximum rate of pressure change is used as a measure of reaction rate is explained by the fact that much of the oxygen is consumed before the maximum rate of pressure change is attained. In contrast to the behaviour of propylene and butene-2, with hexene-1 there is no measurable induction period in the usually accepted sense. Polymerization reactions

are postulated as predominating over oxidative degradations in the early stages of the reaction, particularly when the olefin is present in excess, resulting in a decrease in pressure which precedes the rapid increase in pressure.

### NIKOLAI SEMENOV

N. SEMENOV, Academician of the Academy of Sciences of the U.S.S.R., who was awarded the Nobel Prize for Chemistry in 1956 jointly with Sir CYRIL HINSHELWOOD, F.R.S., has recently been elected a Foreign Member of the Royal Society. He first became recognized as an eminent contributor to the theory of combustion processes when he propounded in 1930 the principle of 'degenerate' or delayed branching in chain processes. His book, *Chemical Kinetics and Chain Reactions*, published by the Oxford University Press in 1935, is a classic on the subject. Semenov is now director of the Institute of Chemical Physics in Moscow and his most recent work has been concerned with the isomerization and reactions of free radicals.

### NEW ANTIKNOCK AGENT

Ethyl Corporation have announced a new antiknock agent, methyl *cyclo*-pentadienyl manganese carbonyl, a light amber liquid, called AK–33X. Though the compound is not yet commercially available, the Corporation has suggested that the petroleum industry should assume a price of 0·85 cent per gramme of manganese. At this price the new antiknock agent would cost four times as much as tetraethyl lead on the basis of metal weight. On the other hand, AK–33X is more effective in increasing octane number per unit of metal weight than tetraethyl lead. The new agent apparently can be used to the best advantage in conjunction with tetraethyl lead [*Chem. Engng* 65 (19 May 1958) 60].

### FUEL FLOW AND COMBUSTION

A conference on the combustion of fuels and flow conditions in combustion chambers and burners was held in October 1957 in Freudenstadt, organized by the V.D.I.–Fachgruppe Energietechnik, and under the direction of Prof. Dr-Ing. F. BOŠNJAKOVIĆ and Prof. Dr-Ing. R. WILLE, chairmen of the V.D.I. Committee for heat and flow research. Fourteen papers, five of which were from countries other than Germany, were presented and these have now been published together with the discussions in a special issue of *Brennst.-Wärmekr.* [10 (1958) 257 to 299]. The papers are divided into four groups: (*i*) atomization and drop size distribution; (*ii*) flame formation, diffusion and conditions in the boundary layer; (*iii*) experiments with models and full size combustion chambers and furnaces; (*iv*) extreme conditions of time, velocity and temperature.

A paper by R. KLING, of the Office National d'Etudes et de Recherches Aéronautiques (ONERA), describes the application of high-speed micro-photography to the investigation of fuel sprays and flow conditions in combustion chambers of jet propulsion units. A method was devised whereby it was possible to determine the statistical composition of the fuel mist and the course of individual droplets. From the relationship obtained

between the average Sauter-diameter and the degree of combustion it appears that the type of atomization has little influence on the combustion efficiency. Consequently an essential improvement in the performance of such combustion chambers at low loads and high altitudes can be expected only from the use of new fuels or fuel additives.

The measurement and description of drop size distribution is discussed by E. KLEIN of the Deutsche Versuchsanstalt für Luftfahrt e.V., Institut für Turbulenzforschung. The conditions for obtaining a representative sample for the evaluation of drop size distribution in a spray are generally not realized even for direct measuring methods. With the immersion method of measuring drop size distribution an improvement can be achieved by directly centrifuging all drops contained in a sector of the spray. A description is given of the method used and of how the sector of the spray is separated by a spray-diverter which is operated by a rapid shutter mechanism. It is shown that on reducing the measured drop distribution to a standard distribution a pair of values can be obtained which represent the atomization. With these two parameters changes of distribution with changing operating conditions can be clearly represented.

Theories which have been put forward to explain the effectiveness of flameholders on the stabilization of flames are examined in a paper by I. SURUGUE, of ONERA. Individual flame zones were either coloured or made visible by the shadow or schlieren method. Lines of equal $CO_2$- or CO-contents were determined by localized gas analyses and CH and $C_2$ radicals were determined by spectrography. A picture was obtained of the aerodynamic and combustion conditions behind the flameholder which corresponds to a combination of the theories of J. P. LONGWELL [*Fourth Symposium (International) on Combustion, Flame and Explosion Phenomena*, p 90. Williams and Wilkins: Baltimore, 1953; *Combustion Researches and Reviews*, p 58. AGARD; Butterworths: London, 1955] and A. MESTRE [*Rech. aéro.*, No. 41 (1954) 23; *Combustion Researches and Reviews*, p 72. AGARD; Butterworths: London, 1955].

F. FETTING, A. P. ROY CHOUDHURY and R. H. WILHELM describe an investigation sponsored by the United States Air Force on the effect of the addition of small amounts of auxiliary gases on the stabilization limits of turbulent flames stabilized by flameholders. Characteristic shifts of the stabilization curves were found to occur with different fuels as well as with oxygen used as auxiliary gas. These results are discussed in the light of complementary investigations made on the influence of the shape of the flameholder on the stability of the flame. Schlieren photographs of the flow round the flameholder appear to indicate that small boundary areas in the wake, particularly near the holder, are essential for stabilization.

## PARIS CONFERENCE ON COMBUSTION OF FUELS

A conference on the combustion of solid and pulverized fuels was held in Paris in December 1957 organized by l'Institut Français des Combustibles et de l'Energie and a review of this has recently been published by G. G. THURLOW [*Mon. Bull. Brit. Coal Util. Res. Ass.* 22 (1958) 165]. Over forty papers were presented dealing with coal preparation, characteristics of

coals used in combustion, mechanism of the combustion of solid an pulverized coal, combustion plant, control, testing and boiler availabilit

An interesting point noted in connection with the preparation of coal is the development of a theory for washing in which the yield from an washing process is related to the density of the material. A coefficient is inserted dependent solely on the method of washing used, and values fo this are given for various plants.

In the discussion on the mechanism of the combustion of solid an pulverized coal, it was pointed out that it is essential to consider a flame as a whole and that the problem can really only be dealt with statistically. In the combustion of pulverized coal the differences between the volatile and coke-burning parts of the fuel, the effect of particle size on the rate of combustion, the determination of the relevant surface areas of the particles, the influence of the internal surface area, and the formation of cenospheres all require further consideration.

With regard to combustion chambers for burning pulverized fuel, it was stated that in firing dry-bottom furnaces it is preferable in practice to keep the primary air low with coals of less than 17 per cent volatiles in order to obtain rapid heating of the fuel entering the combustion chamber. A higher primary air rate is preferable with richer coals. With the dry-bottom furnaces, the disposal of ash presents a serious problem with high-ash coals.

In the firing of rotary cement kilns most of the heat was said to be transferred by radiation and not convection and some experimental results indicated that whilst the radiation from the flame decreased with increasing primary air, the output from the furnace increased. It was suggested that this may be due to the action of *convection vive*, but a satisfactory explanation is not yet forthcoming.

In considering large and medium sized combustion installations, for fuels other than pulverized, a stoker was described which consists of a conventional travelling grate with the pneumatic injection of part of the fuel over the top. Two different fuels could be used in this way and it suggests that this method of firing may be a means of burning fuels with a high proportion of fines.

A novel method was described for burning a lignite containing some fossilized wood and with a large water content. A pulverized fuel unit was combined, at the bottom of the combustion chamber, with a gas producer unit. Fuel dropping during the pulverized-fuel firing falls into the gas producer unit and the gases are burnt in the furnace proper. By this means an overall efficiency of more than 85 per cent can be achieved.

## FIRE RESEARCH 1957

Plans for the permanent Fire Research Station of the Department of Scientific and Industrial Research and the Fire Offices' Committee at Boreham Wood, Herts, have now reached an advanced stage and it is hoped that building will begin this year. Until now, the station has been making-do with temporary laboratories that are not well suited to all the needs of practical investigations of fire. The exception to this is the well-equipped furnace building now in use and a models laboratory in course

of rection. This is stated in the report of the Fire Research Board for 195[illegible] recently published (*Fire Research 1957*, published for the D.S.I.R. and Fire Offices' Committee by Her Majesty's Stationery Office, 1958).

Amongst the researches reported is work carried out at the Safety in Mines Research Establishment at Buxton in connection with the hazard of coal dust explosion in the operation of grinding mills for the preparation of pulverized fuel for firing modern steam boilers. An investigation into explosion-relief venting to prevent dangerous pressures from being developed in such mills is now in progress at the request of the Central Electricity Generating Board, and a coal pulverizing mill has been erected for use as an experimental explosion vessel. It has been found that using a small flame inside the mill as the source of ignition, and with venting consisting of a single unobstructed opening 1·5 ft² in area, a dust explosion caused a violent projection of flame to a height of about 20 ft, but the pressure developed was low and insufficient to damage the mill.

Work on the problem of the suppression of homogeneous combustion by inhibitors is being carried out in the University of Oxford under the supervision of Sir CYRIL HINSHELWOOD, P.R.S. The results to date relate to the interaction with oxygen of hydrocarbons of the *cyclo*paraffin series in the vapour state. The ease of oxidation is found to be extremely sensitive to structure, increasing very markedly with the number of carbon atoms but being quite strongly depressed by substitution of methyl groups. There is a long induction period preceding establishment of the maximum reaction rate. The rate/concentration relations are somewhat unusual. The rate rises steeply with increase in hydrocarbon concentration to a point where an ignition limit is reached. Depending on the hydrocarbon pressure the rate either rises steeply with oxygen pressure or reaches a limit beyond which the oxygen pressure has no further effect. In other words, excess oxygen in some circumstances has virtually an inhibiting action. An observation which suggests developments of practical interest is that the length of the induction period can be very considerably modified by the addition of aldehydes. Aldehydes are probably intermediates in the reactions and they are susceptible of catalytic destruction. Consequently it may be expected that certain additives would greatly prolong induction periods and so substantially diminish the ease of ignition.

## FLAME RADIATION IN HIGH INTENSITY COMBUSTION SYSTEMS

D. J. WEEKS and O. A. SAUNDERS, F.R.S., have published a paper relating some studies of radiating flames in a small gas turbine type combustion chamber which were carried out in the Department of Mechanical Engineering, Imperial College of Science and Technology, London [*J. Inst. Fuel* 31 (1958) 247]. The combustion chamber, of the swirler type, burned 30 lb of fuel per hour at approximately atmospheric pressure, giving a combustion intensity of 280 000 C.H.U. per ft³ h. Three fuels were used, kerosine, a light oil blend, and the heavy Admiralty 'mothball' fuel. Total and spectral radiation and absorption were measured. The two former fuels gave very little luminous radiation, but the heavy fuel gave a considerable amount.

In the centre of each flame near the burner there was a core of unburnt

fuel which burnt away with increasing distance from the burner. Although this core did not radiate appreciably, being relatively cool, it absorbed strongly and affected measurements such as those by the Schmidt method which depends on measuring absorptivity. The distribution of composition and temperature across the flame width was very far from being uniform near the burner and care is required in defining effective temperature, emissivity and absorptivity and in interpreting the results of these measurements. The authors consider that the highly-absorbing cold core causes the Schmidt method to give an artificially high emissivity and low temperature though correct total radiation. Spectral measurements may be completely misleading. The luminous radiation, unlike the non-luminous, is shown to depend on the detailed flame structure. Some extrapolation of the results to larger sizes of combustion chamber and higher absolute pressures may be possible, but the general problem of calculating the luminous radiation for any given burner arrangement and fuel is still unsolved.

### FLOW FIELD OF A BUNSEN FLAME

When a flame is stabilized at suitable boundaries and the combustible gases stream through it, the dynamics of the flow determine to a large extent the structure and stability of the flame. A recent contribution to our knowledge of this subject has been made by M. S. Uberoi, A. M. Kuethe and H. R. Menkes, of the University of Michigan, who have examined the flow field of a two-dimensional bunsen flame [*Physics of Fluids*, 1 (1958) 150]. The method used is to approximate the zone of combustion by a surface of discontinuity across which the density drops and the velocity normal to the flame at every point increases. Although the flow changes induced by the flame in the unburnt region are potential, the flow in the burnt gases is always rotational and this constitutes a difficulty in obtaining a complete analysis as there are no analytical methods for solving rotational flows. Numerical methods, therefore, must be used but these do not give sufficient insight into the mechanism of such flow. However, in an attempt to resolve this difficulty the present authors have considered the effect of tangential velocity at the flame front since it determines the vorticity in the burnt gases, and also the effect of flame front curvature. Interaction of flame shape and flow field was obtained both analytically and experimentally. The entire flow field of unburnt and burnt gases was mapped by taking stroboscopic photographs of small particles suspended in the combustible gases.

### FORMATION OF ACETYLENE FROM METHANE

Z. V. Ievleva and P. A. Tesner have investigated the formation of acetylene by the partial combustion of methane in oxygen [*Trud. vsesoyuz. nauch.-issled. Inst. Prirod. Gaz. (Proc. Union sci.-res. Inst. Nat. Gas U.S.S.R.)*, 1 (9) (1957) 100–122]. The process was studied in a bunsen type flame and a heated tube. In either case a sharp division into two stages was observed, rapid combustion, followed by a relatively slow reaction. The greater part of the acetylene is formed in the zone of rapid combustion and immediately beyond this zone the water gas equilibrium is

established. With oxygen at atmospheric pressure the maximum yield of acetylene is determined mainly by the ratio of methane to oxygen in the original mixture. Combustion of a mixture of methane and propane produces more acetylene than pure methane.

### HIGH FLAME TEMPERATURE

The combustion of cyanogen in oxygen is of special interest as it provides one of the highest flame temperatures obtainable by chemical means. The equation

$$C_2N_2\,(g) + O_2\,(g) \rightarrow 2CO\,(g) + N_2\,(g)$$

represents the simplest possible stoichiometric relation for the combustion of cyanogen. The heat of reaction at 298° K is 126 680 cal and in view of the fact that the products of the reaction are extremely stable, a very high flame temperature is to be expected. This reaction has recently been further investigated by J. B. CONWAY and A. V. GROSSE, of the Research Institute of Temple University, who have also described a technique for operating this flame at elevated pressures to give increased flame temperatures [*J. Amer. chem. Soc.* 80 (1958) 2972]. These investigators have measured the cyanogen–oxygen temperature at atmospheric pressure using the lithium line-reversal method with the sun as the comparison radiator. The flame temperature for the above reaction was found to be 4 640° K, which is in fairly good agreement with the calculated flame temperature of 4 835° K, providing additional evidence in favour of the high value of $\Delta H^{\circ}_{\mathrm{d}} = 226\,000$ cal per mole for the dissociation of nitrogen.

### BURNING VELOCITY OF GAS BY CONSTANT-VOLUME METHOD

The two methods of determining the burning velocity of a gas mixture, the constant-pressure soap bubble method and the method using a stationary flame on a burner, have been critically examined in recent years by several investigators, particularly J. W. LINNETT and his co-workers. A comparison, however, between the constant-volume method and other methods does not appear to have been made, probably because the results available for the former method are limited in number and also because of the complications due to the variations in pressure during combustion. The method has now been examined by K. H. O'DONOVAN and C. J. RALLIS, of the Department of Mechanical Engineering, University of the Witwatersrand (*Report No. 1/58*, May 1958).

A method of determining burning velocity from constant-volume explosions in a spherical vessel was developed by E. F. FIOCK, C. F. MARVIN, F. R. CALDWELL and C. H. ROEDER [*Nat. Adv. Comm. Aero. Rep. No. 682* (1940)]. The equation formulated was later modified by B. LEWIS and G. VON ELBE but it was applicable only to the early stages of combustion in which the pressure is low. The analysis made by these investigators has been re-developed in the present paper to provide an accurate means of determining the burning velocity under constant-volume conditions. The approach is that of deriving an exact equation for the mass fraction burned at any instant during combustion, valid throughout

the combustion period. This involves a consideration of the temperature distribution in the vessel at any instant. Pressure/time and flame radius/time experimental records are required. The analysis proposed permits full use to be made of the chief advantage of the constant volume method, which is that the burning velocity may be found over a large range of pressures in a single explosion.

### NATIONAL CHEMICAL LABORATORY

The Lord President of the Council has approved changes in the functions of the Chemical Research Laboratory, Teddington, Middlesex, proposed by the Council for Scientific and Industrial Research. In addition the name of the Laboratory will be changed to the National Chemical Laboratory.

The Laboratory will concentrate its effort on a few objectives, covering only a limited part of the whole field of chemical research, so as to be able to make a real impact on selected problems of national importance such as: the determination of the fundamental physicochemical properties of chemical compounds which are required, for example, by chemical engineers for the design of full-scale industrial plant; the study of the development of techniques of purification of materials such as metals and chemicals, with a view to the supply of standard samples of pure substances for reference purposes; fundamental and applied studies of the corrosion of metals; the extraction of elements of atomic energy interest from low grade ores.

### CONVECTION VIVE

J. DUMORTIER, Ingénieur au Conservatoire National des Arts et Métiers (C.N.A.M.), has recently published a thesis that he presented to the Faculty of Science in the University of Paris, for the degree of Ingénieur-Docteur, on the combustion of small quantities of carbon monoxide capable of generating *convection vive* in contact with steel walls [*Flamme et Thermique*, 10 (1958) (No. 116) 13, (No. 117) 33].

The different amounts of superheat obtained in steam boilers of the same size and operated under similar conditions but differing in the metal used for the superheater, led Professor M. VERON of the C.N.A.M. and l'Ecole Centrale des Arts et Manufactures, to think that this might be due to surface *convection vive* due to the combustion of traces of carbon monoxide. Consequently an investigation, described in this paper, was carried out to study the catalytic combustion of traces of carbon monoxide which are outside the limits of inflammability and at temperatures clearly below 650° C, usually recognized as the temperature of ignition.

The experimental equipment consisted essentially of a silica or glass tube which could be packed with steel spirals or turnings, and through which air could be passed containing carbon dioxide and varying amounts of carbon monoxide, 0·5 to 2 per cent, such as are found in boiler practice. The tube was heated to different temperatures and the exit gases were analysed for content of carbon monoxide, varying the temperature, time of contact with the packing surface, and the nature and amount of surface exposed.

From the experimental results relationships have been formulated to express the relative content of carbon monoxide as a function of these variables, the relative content of carbon monoxide being the ratio of the percentage content of CO in the exit gases from the furnace to the original percentage CO content.

## RADIANT HEAT EXCHANGE IN A FURNACE

H. C. HOTTEL and E. S. COHEN, of the Massachusetts Institute of Technology, have recently published an important paper presenting a method for predicting radiant heat interchange in enclosures where allowance has to be made for gas-temperature variation [*Amer. Instn chem. Engrs Jnl* 4 (1958) 3].

The methods available at present for calculating the performance of a furnace of specified shape and size, fed with fuel and air at specified rates and in a specified pattern, allow determination of the details of surface-temperature variation and surface-heat flux variation for the special case of an assumed uniform temperature and composition of the gases in the furnace enclosure. The objective of the present work is to advance a stage farther towards a general solution by removing the restriction of gas-temperature uniformity and to establish, in the course of the solution, space variation both in surface and in gas temperatures. The analysis is limited to a solution of the heat transfer problem, information about the combustion and mixing patterns in the furnace enclosure being assumed available.

The system is divided into surface zones and gas zones, the number being dependent on the desired accuracy of the result. Direct-exchange factors are available for gas–gas, gas–surface, and surface–surface zone interchange. From these factors the net exchange factor for any zone pair can be determined, making allowance for interaction with all other zones. The resultant factors are then fed into a set of energy balances, one on each zone, which by simultaneous solution permit a determination of the space distribution of gas and surface temperatures and the distribution of heat flux over the surface.

The new technique is said to be capable of solving far more complex problems than could previously have been handled. An important engineering application of the method is its use on a particular model or class of furnaces in comparison with various engineering short cuts, to determine the range over which one of them may be relied upon.

## AGARD COLLOQUIUM

The Combustion and Propulsion Panel of AGARD (Advisory Group on Aeronautical Research and Development to NATO) held its third Colloquium at Palermo, Sicily, during 17 to 21 March 1958. Eighteen invited papers were presented with prepared comments from forty five selected reviewers. The papers were grouped under the following headings: (*i*) power plant requirements related to aircraft mission, (*ii*) interaction of combustion systems with other engine components, (*iii*) noise, (*iv*) combustion, (*v*) aerophysical chemistry.

One of the papers, presented by G. RUDINGER, of the Cornell Aeronautical Laboratory, New York, is concerned with a theoretical analysis of pressure wave and flame front interaction as evidenced in photographic records obtained by several investigators and in particular by G. H. MARKSTEIN. Pressure waves, which are generated in the burning zone during the propagation of flame in cylinders, influence the course of combustion by their interaction with the flame after reflection from the ends of the cylinder. Oscillations of considerable magnitude may be set up.

When a pressure wave strikes a flame front, in addition to waves which are very rapidly produced, transmitted and reflected, there are pressure waves emitted from the flame for a short time after impact. The explanation of this phenomenon appears to have been provided by schlieren photographs illustrating the disruption of the flame surface due to the short acceleration. The associated increase in the surface area of the flame produces a corresponding increase in the rate of combustion which is accompanied by the emission of secondary waves. The formation of such secondary waves is particularly noticed in very highly turbulent flames.

D. B. SPALDING, of the Imperial College of Science and Technology, London, in a paper on recent progress in flame theory, formulated seven *useful half-truths* (u.h.t.s) as sufficiently compact, general, and factual, to be valuable for combustion engineers in designing, as alternatives to the excessively long-winded statements which are necessary for expressing true statements about combustion processes. The first two of these u.h.t.s refer to *aerodynamic* and *mixing* aspects, in connection with the use of water and two-fluid models for the study of flow in combustion chambers. The third relates the state of the local gas mixture to the local fuel/air ratio and the local reactedness, while the fourth emphasizes that reaction rate depends only on the instantaneous state of the gas. The fifth u.h.t. is concerned with the predictability of the performance of combustion systems from small scale models operating at different pressures. The sixth u.h.t. is used in various forms to correlate experimental data on combustion performance. The seventh u.h.t. provides a basis for the *influence coefficient* approach to flames.

The author considers there are three outstanding tasks in this field. The engineer should investigate whether a fully premixed charge is superior to separate injection of fuel and air, the aerodynamicist should study turbulent flows involving simultaneous jet-mixing, recirculation and chemical reaction, and the chemist should devise simple flame arrangements to give results which are amenable to theoretical analysis and differ greatly according to the reaction-kinetic scheme involved.

## NUCLEAR FUEL CYCLES

A symposium is to be held in London on 'Nuclear Fuel Cycles' on 22 and 23 January 1959, arranged by The Institute of Physics, which is one of the constituent bodies of the British Nuclear Energy Conference.

There will be three sessions dealing with: (*i*) (*a*) long-term reactivity changes, (*b*) theory of once-through fuel cycles, (*c*) perturbations due to

fuel cycles, (*ii*) optimization of fuel cycles for nuclear power stations, (*iii*) fuel cycle operational problems.

The papers to be presented will deal with the applied physics aspects of the fuel cycles which form the basis of the immediate nuclear power programme. Abstracts, but not preprints, of the papers will be available early in January.

Application forms for tickets to attend the symposium are obtainable from the Secretary, The Institute of Physics, 47 Belgrave Square, London, S.W.1, and should be returned as soon as possible.

W. A. KIRKBY

## MECHANISMS FOR THE FORMATION OF IONS IN FLAMES

Readers of *Combustion and Flame* may like to know that the second equation on page 398 of Volume 1 (1957) should read

$$M_1 + OH^- \rightarrow M_1OH^-$$

or

$$\rightarrow M_1OH + e^-$$

It is regretted that an accident occurred when the page was being prepared for printing, and the above equation was suppressed. This correction is published by request of Dr H. F. CALCOTE, author of the article.

## FUEL

Attention is drawn to a *Note* dealing with 'Soviet trends in physical measurement' which appeared in *Fuel* in July.

# *Seventh International Symposium on Combustion—a Brief Survey*

G. J. MINKOFF

The Seventh International Symposium on Combustion, held recently in London and Oxford, maintained the high scientific standard of the earlier conferences. Perhaps the main feature, on this occasion, was the continuous insistence on the detailed interpretation of the various phenomena under discussion. In general, the less precise representations which had been necessary in the past were being discarded, and a much closer attention to details has been replacing them. This trend was noticeable both in theoretical and in experimental papers in fields which included detonation, spectroscopy, mechanisms of reactions, and flame properties. Again, close scrutiny was applied to the precise mode by which energy is exchanged not only between molecules and radicals, but between different types of energy, such as translational, rotational, vibrational and electronic. The magnitude of this achievement is indicated when we realize that fifteen years ago, the papers proving that radicals were involved in pyrolytic reactions were themselves relatively new, and that the discovery of low-pressure explosions had only just preceded the pyrolysis work. A consequence is that much of the earlier work becomes forgotten at too high a rate; much of it, in fact, is re-'discovered' every few years!

The purpose of the organizers, according to the early announcements, was to increase our knowledge of the physics and chemistry of flames. The properties selected for special attention included the details of high speed flame reactions, the application of spectroscopy to flames, the distribution of heat release and of concentrations across flame fronts, the electrical properties of flames, turbulence, shock wave and detonation phenomena, and the application to engineering problems. The papers presented and the discussions both contributed to this aim, the emphasis being on basic new concepts, on new methods and important new data, and on unusual applications. Some comments may be made on the selection of papers and on the mode of presentation. The committee was inundated with papers and they therefore aimed at selecting those which made important new contributions as well as those which were expected to give rise to useful and stimulating discussions. On the whole, there have been few complaints. An important advance was in the procedure in the individual sessions, this having always provided some difficulties at previous symposia. There, the members were only provided with volumes containing 1 000-word summaries of the papers and the authors therefore had to present their papers in some detail, thus reducing the time available for discussion. This year, with the willing co-operation of the publishers, full preprints were available, following the procedure of conferences organized by the Institute of Petroleum, the Faraday Society, etc. It was thus possible to select four or five papers for individual presentation in each session, and to allow only 7 to 8 minutes to each author to emphasize his main points. An 'opener of discussion' was

then called upon, who drew attention to the features which required discussion not only in these four papers, but also in those which were not selected for presentation by their individual authors, but which were available in the volume of preprints. There then remained about half the length of each session available for discussion. There was a wide variety in the interpretation of the role of 'opener', and the innovation appears to be eminently successful. The organizing committee kept the number of overlapping sessions down to four occasions thus reducing some of the frustrations encountered at earlier symposia.

The subject matter, for the purpose of this review, may be divided into four sections, dealing with (*a*) detonation, (*b*) flame structure, (*c*) mechanism of oxidation, (*d*) flame properties and combustion in practical systems. Let us first consider the sessions on various aspects of detonation. Considerable advances have been made here, both experimentally and theoretically. The range of detonatability of hydrogen–oxygen mixtures has been widely measured. Predictions have also been made, based on the known kinetic rates of individual reactions; these are extrapolated from lower temperatures, and the requisite high temperature and pressure conditions necessary are translated into conditions for detonation. The justification for the extrapolation was discussed at some length. The analysis of spinning detonations has also proceeded at a rapid rate, although many of the basic observations were made many years ago. At the same time, it was clear that the description of 'spinning' was being applied somewhat freely, and more specific definitions were called for; for example, if the pressure only was being recorded, the fluctuation could be due either to true spin or to alternation in a standing wave. The role of turbulence was also considered; attention was drawn to the possibilities of confusing variations of flame thickness (shown photographically) due to pressure changes and to different degrees of turbulence.

One of the major accomplishments reported at the Conference was the stabilization of gaseous detonation waves, in two separate laboratories. This opens the way for detailed spectroscopic and optical analyses of the type which have proved so fruitful in connection with studies of the structure of flame fronts. Considerable interest was shown in this elegant way of examining the interaction of flames and shock waves.

From a general point of view, the study of limiting conditions seems likely to prove as useful as it did with flame and explosion limits in unravelling the details of the mechanism of the change from combustion to detonation. Associated with this is the problem of the mechanism of energy exchange, and of the degrees of freedom available, which are readily established for light gases such as hydrogen, but which are not obvious for complex molecules. Even more puzzling (and therefore, eventually, worthwhile) is the mechanism of energy conversion when some of the products are solids such as carbon, boron oxide or other metal oxides. At the same time, the techniques provide a useful tool for the study of rapid, high temperature reactions.

Many aspects of the transition into detonation were considered. It is perhaps worth drawing attention to the confusion which may arise between

the case of flames ignited at the ends of open tubes, acceleration eventually occurring, and the case of spark ignition within a tube, away from an open end. Here, part of the acceleration is due to geometrical factors involving changes of flame envelope from spherical to cylindrical. The role of turbulence was again raised and illustrated. The importance of avoiding reflection of shock waves at interfaces such as that between the explosive and the container was stressed, with suggestions for overcoming this difficulty. The detailed way in which pressure waves from flame fronts can build up into shock waves was discussed, as were the interaction of flame fronts with shock waves. Many beautiful photographs were presented which illustrated the transition, one of the more spectacular sequences involving a liquid explosive. This showed the change in shape of the container as it shattered. In sympathy with the results mentioned below, ions were found to be present in comparatively large quantities.

The second group of papers was concerned with the elucidation of the structure of flame fronts, with particular reference to rates of heat release and the changes in composition in the gases approaching the burning zone. The studies of the electrical properties of the flames, and of the processes leading to the attainment of equilibrium in the hot gases, also fall into this category. As in so many other researches, the availability of flat flame burners has greatly facilitated this type of approach, although candle flames have also been investigated. The general results support the growing realization that much of the fuel has decomposed before the flame front has been reached, and observations with a bearing on the mechanism of carbon formation have been reported. One of the developments here is the correlation between the low work function of carbon and the high electron concentrations. This suggests the possibility of some of the ionization occurring at the surface of the carbon. The discovery of u.v. absorption bands of benzene below the flames of ether and of hexane is also of great importance.

The concentration profiles are at present being determined partly by overall optical methods, from which the heat release rates can be deduced as a function of distance; partly by sampling through a very narrow probe, the chilled products being then analysed by mass spectrometry or by gas chromatography; and finally by u.v. and i.r. emission and absorption. These are all complementary, for while some methods give more details than others, they may involve disturbing the gases (although this is the subject of some controversy). Again, the spectroscopic methods are complicated by self-absorption and by light-bending effects, but suitable corrections may be made. A possible general source of error is the presence of vortices at the edges, which alter the compositions to some extent. Another is the uncertainty in the position of the true flame front, as distinct from its thickness as viewed. Great strides may be expected in this field.

The unexpected large concentrations of ions have led to several investigations of their identities with mass spectrometers, and wide varieties of ions, including C, H, N and O atoms, have been reported. It is now necessary to establish whether they are a small proportion of side products, or whether they can be a guide to the overall mechanisms. An extreme possi-

bility is that they may be used for studying ion reactions in the absence of a solvent! The recombination processes in flames are also involved. Here, elegant techniques have been developed, in the presence of different metals, which indicate that recombination on some metals may be to some extent specific. Thus, Th is excited by the recombination of H + H, while Pb is associated with the reaction of $H + OH = H_2O$. The stability of possible intermediates was discussed, as was the mode of energy transfer. An entire session was also devoted to this topic, which was concerned both with theoretical calculations and with modern instrumental methods of determining relaxation times. A useful generalization was that the efficiency of a transfer decreases as the amount of energy increases. Several workers have thus found that consideration of rotational levels as well as vibrational may facilitate the process. At the same time, the presence of rotation in a diatomic molecule may well lead to a pre-dissociation through tunnelling, and hence to an increase in dissociation rate. Excitation of high vibrational levels, with only low population in the high rotational levels, is observed in many reactions of the type $A + BCD = AB + CD$. A particularly elegant technique involved the excitation of a vibrationally excited level of CO, in a region which could be easily isolated by filters; the light emission was then followed with a high speed i.r. detector. The interplay of molecular dynamics and reaction kinetics was evident throughout the discussion.

The concern with the details of the exchange of energy was also reflected throughout the papers dealing with combustion mechanisms, principally in connection with the roles of $HO_2$ and of water. The main feature of the developments in this field is the increasing understanding of the mechanism by which surfaces affect chemical reactions. As a result of this work, which now enables us to explain how radicals such as $HO_2$, and even H and O, behave on different categories of coatings, it is convenient to re-examine many of the old and new observations on the oxidation of hydrogen and of methane, now the best understood combustion reactions (though problems still abound!). New slow reactions of hydrogen with oxygen on boric acid surfaces, for example, have resolved the conflict between the ratios of $2k_2/4$ and $3k_2/4$. Here again, the value, and indeed the correctness of much of the early work, should not be overlooked. Other developments include measurements of the lifetime of $HO_2^*$ by various methods, and the application to various combustion processes. The early elimination of such reactions, based on kinetic observations, should nevertheless be remembered. There is obviously scope for much work, which may also seek more direct proof of the existence, in reacting systems, of the radicals whose participation is deduced from the kinetics. Also in this category is the controversy regarding the way in which water assists the reaction

$$M + H + O_2 = HO_2 + M$$

The third body efficiency of water is supposed to be abnormally large and, although this was not universally accepted, many suggestions were discussed for the detailed interaction. Finally, it may be said that although the laboratory experiments on the interaction of metal oxide surfaces with $HO_2$ and $H_2O_2$ seem very convincing, the location of the corresponding process in an internal combustion engine appears to be still unresolved.

General studies of hydrocarbon oxidation mechanisms are proceeding, with the emphasis on precise product analysis and measurement, if possible, of individual reaction rates. A healthy development is in the number of papers devoted to the oxidation of non-hydrocarbons, such as nitrogen derivatives, and also of metal organic compounds. There is scope for much more work here, although the experimental problems are very considerable. An additional difficulty is the apparent absence of likely intermediates for example in the oxidation of boron compounds.

Finally, let us consider the group of papers concerned with flame propagation and allied topics. Here, it appears that an important stage has been reached. Theories of burning velocity can now be checked against flame structure measurements sufficiently for major developments in their use to be foreseeable in the immediate future. Some of the more detailed theories, in fact, are now in sufficiently handleable form for burning velocities to be deduced by calculation almost as readily, in some cases, as by measurement. In the field of turbulent combustion and chamber design, development is assisted by the construction of several types of analogue computers, the performance of which gave rise to considerable discussion. Regarding the future, the need for greater knowledge of the kinetics of high speed, high temperature reactions was stressed. This is required, for example, to assist in determining in individual cases whether overall heat release rates will be controlled by the kinetics or by mixing processes. In this connection, a new theory of turbulent burning received much attention. The role of the enthalpy wave was again discussed, and it was suggested that the title of 'energy hump' was more suitable.

In conclusion, the author wishes to emphasize that without the willing collaboration of his colleagues listed below, this brief survey of the Seventh Symposium could not have been compiled within one week of the termination of the Symposium: Affleck, Eisenklam, Fox, Larsen, Nettleton, Peacock, Pratt, Sallouta, Spokes, Warren and Weinberg.

# *Publication*

## SIXTH SYMPOSIUM (INTERNATIONAL) ON COMBUSTION

Published for the Combustion Institute in New York: Reinhold; London: Chapman and Hall, 1957. *xxv* + 943 pp. $28.00 or 224*s*.

This book contains the texts and discussions of the papers presented at the Sixth Symposium on Combustion, the first to be held under the auspices of the Combustion Institute. The number of topics covered in the Symposium is larger than that in either of the two preceding Symposia. There are in all a hundred and twenty five papers and short summaries of panel discussions on Future Problems in Combustion Research, High Speed Reactions and Flame Stabilization in Fast Streams. The largest group of papers is that of thirty seven on ignition and flame phenomena in homogeneous combustion systems. An introductory paper by VON KÁRMÁN summarizes the present position in the theory of laminar flame propagation. The other papers in this group present new contributions on the various aspects of the problem, ranging from further attempts to simplify or solve the equations for laminar flame propagation to experimental investigations of the effects of various parameters on flame phenomena.

The six papers on the structure and propagation of turbulent flames represent further advances in this field, but as yet no certainty is possible as to the structure of these flames. There are eight papers each on high speed reactions and flame stabilization in fast streams, four papers on instability in combustion chambers and five on ignition of gas mixtures. A summary by ORNING of the solid fuel combustion section introduces seven papers dealing with carbon combustion fundamentals, fuel bed combustion and pulverized coal flames. In addition there are eleven papers on the combustion of explosives and solid propellants, nine on the evaporation and combustion of droplets and sprays including a survey by KUMAGAI, nine covering experimental and analytical techniques and twenty in the final section on the applications of combustion.

The papers in general are of a high standard, but a few, apart from the invited surveys and summaries, do cover ground previously reported. The book is excellently printed on high quality paper and as a result of its contents is indispensable to any worker in the field of combustion research and application.

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# *Letters to the Editors*

*Letters to the Editors on points of scientific interest related to combustion and flames are invited. The Editors do not hold themselves responsible for opinions expressed in correspondence. Anonymous contributions cannot be accepted.*

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## *A Note on Spalding's Centroid Formula*

D. B. SPALDING presented in his paper on 'One-dimensional laminar flame theory for temperature-explicit reaction rates' [*Combustion and Flame* 1 (1957) 296], a remarkable formula, namely

$$\lambda = 0{\cdot}5 - 0{\cdot}6604\,(1 - \tau_c) - 0{\cdot}4288\,(1 - \tau_c)^2$$

This formula was obtained by curve fitting a plot of the mass-flow parameter $\lambda$ (properly non-dimensionalized) against the centroid of the reaction rate function $\tau_c$. The existence of a practically universal function $\lambda = \lambda(\tau_c)$ would lead one to believe that the function $\lambda(\tau_c)$ or at least a reasonable facsimile thereof ought to be obtainable from the differential equations by some direct method. The fact that the centroid is defined by an integral presents a clue for the procedure to be followed.

The basic differential equation in Spalding's notation is

$$p\,\mathrm{d}p/\mathrm{d}\tau - p = -\lambda\Phi(\tau)$$

where

$$p = \mathrm{d}\tau/\mathrm{d}x,\quad \tau = (T - T_u)/(T_b - T_u),\quad \lambda = \int_0^1 p\,\mathrm{d}\tau,\quad \Phi = R(\tau)/\int_0^1 R(\tau)\,\mathrm{d}\tau$$

In order to evaluate $\lambda$ we integrate by parts

$$\int_0^1 p\,\mathrm{d}\tau = [p\tau]_0^1 - \int_0^1 (\mathrm{d}p/\mathrm{d}\tau)\,\tau\,\mathrm{d}\tau$$

the first term vanishes on account of the boundary conditions and from the differential equation we get for $\mathrm{d}p/\mathrm{d}\tau$:

$$\mathrm{d}p/\mathrm{d}\tau = 1 - \lambda\Phi/p = 1 - (\Phi/p)\int_0^1 p\,\mathrm{d}\tau$$

Consequently

$$\lambda = \int_0^1 p\,\mathrm{d}\tau \;.\; \int_0^1 (\Phi/p)\,\tau\,\mathrm{d}\tau - \int_0^1 \tau\,\mathrm{d}\tau$$

From a trivial application of the Mean Value Theorem of the Integral Calculus we obtain

$$\int_0^1 p\,\mathrm{d}\tau = p(t_1)\int_0^1 \mathrm{d}\tau \qquad 0 \leqslant t_1 \leqslant 1$$

and similarly

$$\int_0 (\Phi/p)\,\tau\,\mathrm{d}\tau = [1/p(t_2)]\,\tau_c \qquad 0 \leqslant t_2 \leqslant 1$$

This operation is clearly permissible in view of the convergence of the improper integral. We now set $p(t_1)/p(t_2)=a_\Phi$ and

$$\lambda = a_\Phi \tau_e - 0{\cdot}5$$

$a_\Phi$ by virtue of its definition is related to the particular reaction rate function and also to the functional form of the relationship between $p$ and $\tau$ (see *Figure 1*). The fact that $a_\Phi$ turned out to be almost a constant could have been inferred *a priori* by the following heuristic argument. Since $\lambda = \int p \, d\tau$ it follows that $\lambda \leqslant 0{\cdot}5$ (see D. B. SPALDING, *loc. cit.*, page 299, *Figure 1*). The magnitude of $\tau_e$ depends strongly on the temperature at which the bulk of the reaction takes place; call that temperature $T_m$. Now this temperature is very rarely much less than the final temperature. Since the reaction rate

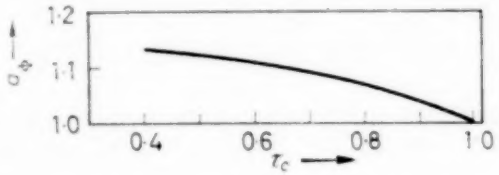


*Figure 1. Variation of a with* $\tau_e$

function is practically symmetrical about $T_m$ it follows that $\tau_e$ is not going to be much different from $\tau_m$ (see Appendix). As a result of that $(\lambda + 0{\cdot}5)$ as well as $\tau_e$ are both of the same order of magnitude, and moreover as $\tau_e$ decreases so does $\lambda$ (i.e. the bulk of the reaction takes place at a lower temperature) (see *Figure 2*). Thus $a_\Phi$ turns out to be the ratio of two quantities that are of the same order of magnitude and that show the same dependence on a common parameter, i.e. $\tau_m$. Inspection of Spalding's *Figure 4* substantiates the soundness of the argument presented. Up to a value of $\tau_e \simeq 0{\cdot}8$ no differences in the various curves can be detected. From there on the differences while still small become quite noticeable. In

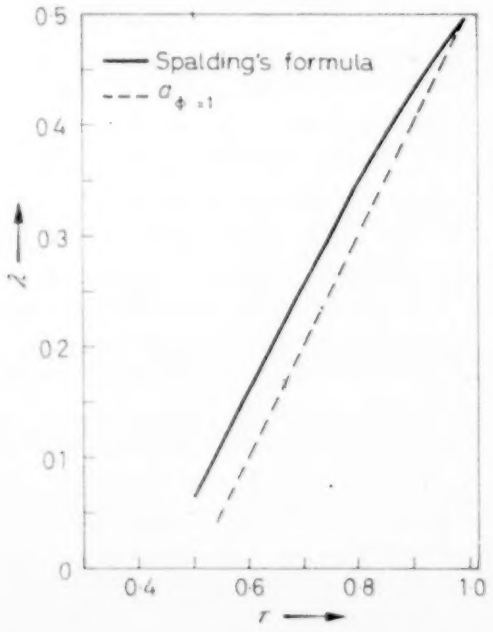


*Figure 2*

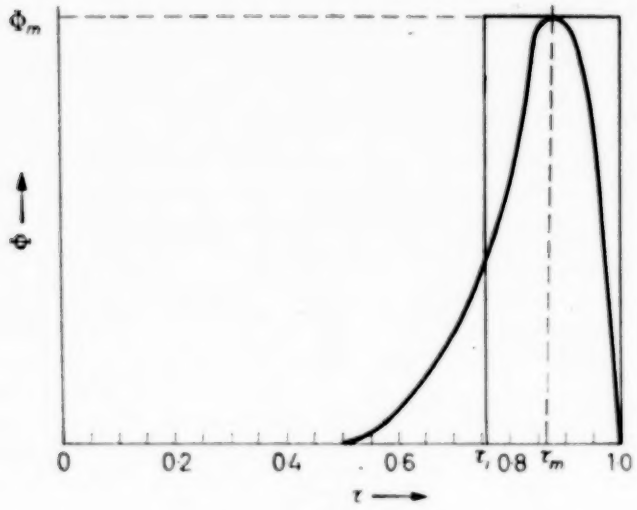


*Figure 3*

conclusion it is desired to point out that the purpose of this note is not to present a better correlation formula (which it does not) but to provide a better than intuitive basis for the existing one.

*The author would like to acknowledge helpful discussions with Dr F. H. Wright and Mr Mitchell Gilbert.*

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*(Received July 1958)*

APPENDIX

We approximate the actual reaction rate by a straight line approximation (see *Figure 3*)

$$\tau_c = \frac{\int_{\tau_i}^{1} \Phi_m \tau \, d\tau}{\int_{\tau_i}^{1} \Phi_m \, d\tau} = \frac{\frac{1}{2}(1-\tau_i^2)}{1-\tau_i} = \frac{1}{2}(1+\tau_i)$$

However, $$\frac{1}{2}(1+\tau_i) \leqslant \tau_m$$

## *Note on Monochromatic Radiation Pyrometry for Measuring Flame and Exhaust Gas Temperatures*

IN recent years there has been considerable interest in the measurement of flame temperatures by means of infra-red (i.r.) radiation. The monochromatic radiation method[1] appears to be a basic approach for practical flame radiation pyrometry. This method has been employed with modern equipment[2–5], and good results have been obtained in measuring average flame temperatures. Very recently the determination of flame temperature gradients by i.r. radiation has become a practical possibility[4, 6].

A recent note in this Journal[7] refers to a method of flame radiation pyrometry described under the name 'Schmidt method' in a paper by R. A. SHERMAN[8]. The method described in Sherman's paper is an extension to flames of total radiation pyrometry, which is commonly used to measure temperatures of solids. This method is based on the Stefan–Boltzmann

law of the continuous blackbody spectrum, which states that the energy radiated is proportional to the fourth power of the absolute temperature. As pointed out by Sherman, the total radiation method can be applied only to grey flames, i.e. flames having a strong continuous spectrum with emissivity independent of wavelength. This restricts the use of the total radiation method to flames containing substantial amounts of carbon, since it is the carbon, not the flame gases, which contribute the continuous grey spectrum. Flame gas radiation, such as that of a bunsen flame[9], consists only of the characteristic emission bands of the gas molecules. The purpose of this note is to point out that flame and exhaust gas temperatures can be obtained readily by means of the monochromatic radiation method irrespective of whether the flame is grey or not, and regardless of whether the hot gases are luminous.

The i.r. monochromatic radiation method is based on the Planck radiation law and Kirchhoff's law. The basic principles of the method are as follows. Using Schmidt's notation[1], the radiation $E_3$ of the flame is measured at a particular wavelength $\lambda$, by means of an i.r. spectroradiometer; and the radiation $E_1$ of a continuous radiator, such as a Nernst glower, is measured at the same wavelength, in the absence of the flame. Lastly, the radiation from the continuous radiator is measured through the flame; this composite radiation $E_2$ consists of flame radiation $E_3$ plus the transmitted (unabsorbed) portion of $E_1$. In the form of an equation, we have

$$E_2 = E_1(1 - A) + E_3 \quad \ldots . [1]$$

where $A$ is the spectral absorptivity of the flame at wavelength $\lambda$. Solving equation 1 for the absorptivity $A$, we get

$$A = \{E_1 - (E_2 - E_3)\}/E_1 \quad \ldots . [2]$$

Applying Kirchhoff's law, which states that the spectral emissivity $e$ of a thermal radiator equals its absorptivity $A$ at the same wavelength and temperature, we have

$$e = (E_1 - E_2 + E_3)/E_1 \quad \ldots . [3]$$

The radiation at wavelength $\lambda$ from a blackbody at the same temperature as the flame is

$$E_b = eE_3 \quad \ldots . [4]$$

where $E_b$ is the Planck radiation function,

$$E_b = c_1\lambda^{-5}(\varepsilon^{c_2/\lambda T} - 1)^{-1} \quad \ldots . [5]$$

The temperature of the flame can be determined from equation 5 once $e$ and $E_3$ have been measured.

In many cases $e$ is independent of temperature[6]. When this condition obtains, the predetermined value of $e$ can be substituted into equation 4. The need for a continuous radiation source behind the flame is thereby obviated.

Equation 2 is the equation at the bottom of page 1008 of Schmidt's paper. The first equation on page 1730 of Sherman's paper is formally similar to equation 3. However, the radiation quantities in Schmidt's

equations represent values measured at a selected narrow band in the i.r. emission spectrum of the flame, while in Sherman's equations the radiation quantities refer to total radiation, as defined by the Stefan–Boltzmann law.

In applying the i.r. monochromatic method, the wavelength used is selected according to the nature of the gas emission spectrum. The strong 2·8 and 4·3 micron bands, characteristic of hydrocarbon flames, are often used.

A particular advantage of using the Planck radiation law, equation 5, is that this usage conforms to the definition of the International Temperature Scale[10], for temperatures above 1 063°C.

By the use of modern electronic equipment, monochromatic gas radiation pyrometry has been adapted to automatic recording, whereby equations 3 and 5 are effectively incorporated in the instrument calibration[3]. The effect of radiation from hot walls behind the gas has been eliminated by means of electro-optical techniques[11] which discriminate between the discontinuous emission spectrum of the hot gases and the continuous background[6].

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(*Received July 1958*)

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